Implications of Oxidation on the Colloidal Stability of Magnetite Nanoparticles and Clusters

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Robert L. F. Rebodos

ABSTRACT

Synthetic nanomagnetite has been suggested as a potential reactant for the in-situ treatment of contaminated groundwater. Although the application of nanomagnetite for environmental remediation is promising, a full understanding of its reactivity has been deterred by the propensity of the nanoparticles to aggregate and form clusters. To characterize the factors responsible for this aggregation behavior, we determined the magnetic properties of magnetite using a superconducting quantum interference device (SQuID). Importantly, because magnetite readily reacts with O$_2$ to produce maghemite, we analyzed the effect of oxidation on its magnetic properties. We observed that oxidation caused a decrease in the saturation magnetization and the anisotrophic barrier of magnetite resulting in less significant magnetic interactions between particles. Consequently, a decrease in the aggregation of magnetite clusters and a potential increase in stability are expected after oxidation. To support these findings, an extended series of experiments to measure the aggregation and the sedimentation of clusters of unoxidized and oxidized magnetite nanoparticles were conducted. Although the individual particle diameter remained constant after oxidation, the cluster size and the aggregation and sedimentation kinetics of magnetite were determined to be different. Oxidized samples of magnetite tended to have lower aggregation rates and were more resistant to sedimentation. These findings can be used to have a better understanding of the overall fate, transport, and reactivity of nanomagnetite, and to gain new insights on its role as a remediation agent in the subsurface environment.
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Chapter 1 Introduction

Magnetite nanoparticles are ubiquitous in the subsurface environment and can be found as components of weathered clays and soils [1, 2]. In addition, magnetite has been observed to be one of the dominant corrosion products formed in the permeable reactive barriers used for in-situ treatment of contaminated groundwater [3]. Biotically, magnetite can be formed as the metabolic byproduct of a wide range of metal reducing [4] and magnetotactic bacteria [5]. Magnetite within the nanodomain (particle diameter, \( d < 100 \text{ nm} \)) is of particular interest because of its potentially unique properties. It has previously been observed that as the size of a crystal decreases, its atomic, electronic, and magnetic structure are altered [6,7]. These alterations can correspond to significant changes in the physical, chemical, and reactive properties of nanomagnetite relative to bulk (coarse) material. The significance of this phenomenon has been illustrated in studies exploring size effects on reactivity [3-7]

In recent years, synthetic nano-magnetite has been utilized as an effective agent for the treatment of groundwater contaminants and has been used as an effective sorbent for heavy metals due to its high surface area [8, 9]. As a reducing agent, it has been employed for the treatment of different organohalides [10]. The redox properties of magnetite may be attributed to the unoxidized iron species present within the crystal. Magnetite has an inverse spinel crystal structure in which the unit cell is comprised of 32 \( \text{O}^{2-} \) anions, 16 \( \text{Fe}^{3+} \) cations, and 8 \( \text{Fe}^{2+} \) cations. Half of the \( \text{Fe}^{3+} \) ions are tetrahedrally coordinated, while the other half and all of the \( \text{Fe}^{2+} \) are octahedrally coordinated. In the octahedral layer, the adjacent positioning of the \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) cations allows electron hopping via overlapping d orbitals between iron atoms [11]. This activity causes magnetite to have near metallic properties [12]. The magnetic property of magnetite is due to the fact that the spins of tetrahedrally coordinated \( \text{Fe}^{3+} \) and the spins of the octahedrally
coordinated Fe$^{3+}$ and Fe$^{2+}$ are antiparallel and unequal in magnitude [13, 14]. When an external magnetic field is applied below the Curie temperature (850 K), these interpenetrating sublattices align antiparallel with unequal moments resulting in the observed ferrimagnetism.

Although application of magnetite nanoparticles for environmental remediation has proven to be a promising technology, a full understanding and characterization of nanomagnetite’s reactivity has been deterred by the propensity of the nanoparticles to aggregate and become unstable in suspension. In many studies examining magnetite activity, the effects of aggregation have not been fully explored. Magnetite aggregation, due mainly to interparticle anisotropic dipolar attractions, may lead to the formation of large magnetite clusters. The formation of these clusters will not only affect the transport and delivery of the nanoparticles, but also their reactivity due to the potential loss of the specific activity of individual particles [10, 15].

Derjaguin, Landau, Verwey, Overbeek (DLVO) theory is often used to explain and predict colloidal stability [16]. Classic DLVO considers two types of interactions between colloidal particles: electrostatic repulsions between the electric double layers of two particles and attractive Lifshitz-van der Waals forces. The overall potential energy of interaction, $V_T$, can be defined as

$$V_T = V_{vdW} + V_{ES}$$

(1)

where $V_{vdW}$ and $V_{ES}$ are the Lifshitz-van der Waals and the electrostatic double layer energies, respectively. In general, positive $V_T$ values are indicative of stable suspensions, while negative $V_T$ values indicate an unstable suspension. For amphoteric oxides such as magnetite, the presence of non-DLVO interactions such as short-range repulsive hydration forces should also be considered [17]. Furthermore, magnetite nanoparticles with diameter less than $\approx$30 nm can be
assumed to possess a single magnetic domain. In this work, the simple DLVO model was expanded to incorporate both so called non-DLVO acid/base interactions ($V_{AB}$) and magnetic interactions ($V_m$) such that the total interaction energy was defined as:

$$V_T = V_{vdW} + V_{ES} + V_{AB} + V_m \quad (2)$$

In the presence of dissolved oxygen [18, 19] the following oxidation reaction can occur:

$$3 \text{Fe}_3\text{O}_4 + \frac{1}{2} \text{O}_2 + 2 \text{H}^+ \rightarrow 4 \gamma\text{-Fe}_2\text{O}_3 + \text{Fe}^{2+} + \text{H}_2\text{O} \quad (3)$$

One proposed mechanism to describe this oxidation process suggests that when magnetite is oxidized, an outer coating of maghemite develops at the particle-water interface. Further oxidation proceeds via the diffusion of interstitial Fe$^{II}$ to the particle surface, in order to maintain charge electroneutrality [18-21]. The regenerated Fe$^{II}$ surface is then subject to further oxidation and the cycle continues until the particle is completely oxidized. Prior to the work discussed herein the impacts of this oxidation process on the colloidal stability of a magnetite suspension were unknown.

Within the context of equation 2, the experimental focus of the effort presented within this dissertation was to characterize the colloidal stability or instability of suspensions of nanoparticulate magnetite as a function of their oxidation state. **Chapter 2** describes in detail the experimental approach taken. **Chapter 3** discusses experiments conducted using a Superconducting Quantum Interference Device (SQuID) to experimentally measure the magnitude of the magnetic attractive force between particles. The experimental results from these experiments were then used to estimate the magnitude of $V_m$. **Chapter 4** describes the results of an extended series of experiments conducted to measure the aggregation and the sedimentation of clusters of magnetite nanoparticles.
References


Chapter 2 Materials and Methods

The purpose of this chapter is to provide extended descriptions of the materials and methods used for the experiments described in this dissertation. Both Chapter 3 and Chapter 4 were prepared in manuscript form for ultimate submission to peer-reviewed journals. As such, the Materials and Methods sections in each of those chapters are intentionally short and this Chapter provides additional details about the approach taken in this dissertation.

Reagents

Sample preparation, particle synthesis, and particle storage were conducted inside an anaerobic glovebox (Coy Laboratory Products Inc.) with a 95%/5% N₂/H₂ atmosphere. Anoxic water was used for all experiments that were sensitive to the presence of oxygen. Anoxic water was prepared by boiling 2 L of deionized water (> 18.1 MΩ), obtained from a Barnstead Nanopure filtration system, for 30 minutes and then sparging with either argon or nitrogen gas for an additional 30 minutes while boiling continued. The flask was then covered with a rubber stopper and removed from the heating source. After the water had cooled, it was transferred to the anaerobic glovebox. All chemicals used were reagent grade (Fisher Scientific).

Particle Synthesis

Magnetite nanoparticles were synthesized using a co-precipitation method adapted from Vayssieres, et al. [1]. A mixture of 0.1 M ferrous chloride (FeCl₂) and 0.2 M ferric chloride (FeCl₃) was added drop-wise (~1 drop/s) to a well-mixed solution of 1 M sodium hydroxide (NaOH) and 1 M sodium chloride (NaCl). The final ratio of iron solution to base solution was kept at 3:2 to maintain the pH above 12. Polypropylene containers were used to avoid silicate leaching from glass vessels due to the high pH synthesis conditions. Excess salts were removed
by magnetically separating the precipitated nanoparticles and rinsing with argon purged-deionized water 4× or until the pH of the supernatant was in the 7-8.5 range. Particles coated with tetramethylammonium hydroxide (TMAOH) were also synthesized using the same co-precipitation method except 1 M TMAOH was used instead of 1 M NaOH.

To obtain the mass concentration of the stock magnetite suspension, 2 mL of slurry was placed in a pre-weighed container and stored in an oven at 75 °C for at least 24 hours. The final mass of the dried sample was obtained and converted using the Fe₃O₄/Fe₂O₃ gravimetric ratio assuming all Fe₃O₄ was transformed into Fe₂O₃. Weight measurements were done in triplicate to obtain the average magnetite concentration for a given batch.

Because the magnetite stock suspensions were stored over extended periods of time, the mass concentration measurement was performed before using the particles in a given experiment. The particles may also tend to agglomerate during storage requiring rigorous mixing and brief sonication (t < 1 minute) of the stock of magnetite suspension to breakup aggregates and re-suspend the particles prior to sampling. Dried powdered samples were obtained by decanting excess liquid and drying inside the anaerobic glovebox for up to 48 hours. The drying process was facilitated through the use of a dessicant.

**Particle Characterization**

The morphology, size and diffraction patterns of nanoparticulate magnetite, including those suspended in different salt solutions, were characterized using a Philips 420T TEM at 100 kV. The particles were mounted on carbon coated TEM grids and allowed to dry in an aerobic environment for a minimum of 48 hours. Collected images were transferred digitally using a slow scan 3086 × 2056 pixel camera.

Further characterization of the dried powder samples was done using X-ray powder
diffraction using a Rigaku RAPID Curved IP X-ray powder diffractometer with Cu Kα radiation and an image plate detector. To obtain the infrared spectra of the magnetite samples, a Midac M2004 ATR FT-IR spectrometer with a diamond prism was used.

Raman spectra were acquired via an automated confocal Raman and AFM System (WITec alpha500). The magnetic properties of synthetic magnetite were assessed using a 7-T Quantum Design MPMS Superconducting Quantum Interference Device (SQuID) magnetometer. Dried samples were packed between cotton plugs that were placed inside gelatin capsules. Zero field cooled-field cooled (ZFC-FC) loops were obtained from 5 K-300 K in a field of 500 Oe. Hysteresis loops were obtained in fields up to 7 Tesla (70 kOe) at 5 K and 298 K.

The isoelectric point (IEP) of magnetite was obtained by measuring the electrophoretic mobility of a series of aqueous magnetite suspensions with initial pH values ranging from pH 4.5-12 using a Malvern NanoZs.

**Aggregation Studies**

Careful and thorough sample preparation was required to avoid errors in the aggregation studies. Possible impurities which could lead to sample contamination were minimized by cleaning all vessels prior to use. The use of nonionic detergent-based cleaning solution was avoided so as not to leave trace amounts of surfactants on the vessel that may alter the aggregation behavior of the particles. Glassware was rinsed repeatedly with deionized water. All solutions used in the aggregation studies were prepared using deaerated, de-ionized, distilled water (Nanopure®) inside an anaerobic glovebox. To remove suspended particles, dilution water was passed through a 0.1 μm Anotop™ filter.
Dynamic Light Scattering

The aggregation behavior of the synthesized magnetite nanoparticles was studied using a Malvern ALV CGS-3 system. Using the ALV software, the initial size and growth of aggregates were determined from the intensity weighted hydrodynamic radius of the particle/aggregate using second-order cumulant analysis of the dynamic light scattering (DLS) data. Measurements were collected at a 90° scattering angle every 15 seconds for a period of 30-60 minutes and were conducted at room temperature (23-25°C).

Each sample was placed in a new prewashed glass vial, prerinsed with filtered deionized water prior to the addition of suspension. The vial was capped and the outside was wiped with a non-abrasive, lintless paper to remove any contaminants adhered to the sides of the vial. Since size measurements were performed inside a toluene vat, the vial was dipped into a filtered toluene solution prior to measurement.

Aggregation Kinetics

The formation and growth of the aggregates were monitored by measuring the scattered light intensity using the DLS system. To monitor the effect of particle concentration, samples of different particle concentrations (i.e., \(10^{12}-10^{16}\) particles/mL) were prepared using the same stock solution. The particle concentration of the stock solution was obtained using the gravimetric method. The desired particle concentration of a given suspension was obtained through serial dilution. Three mL of each of the new suspensions were then transferred to a sample tube and vortex mixed for 10 seconds before DLS measurements.

The effect of pH on magnetite aggregation was studied by diluting a given volume of the stock to achieve a suspension of \(\approx 10^{12}\) particles/mL. Different dilution waters of varying pH values (i.e., pH 4-10) were used. The dilution water was prepared by adding either 100 mM HCl
or 100 mM NaOH to the desired pH value and filtered with a 0.1 μm filter prior to use.

The effect of the presence of electrolytes (*i.e.*, monovalent and divalent ions) on the magnetite aggregation rate was analyzed by adding different amounts of salt to a given volume of a diluted nanoparticle suspension (~10^{12} particles/mL) and then sonicated for about 30 seconds. Different stock solutions of NaCl, MgCl₂, CaCl₂, and FeCl₂ were prepared using reagent grade salts and deaerated, deionized water and were double filtered with 0.1 μM nylon filters. Each of the salt stock solutions was subjected to DLS measurements and each gave insignificant response. Corresponding amounts of the stock salt solution were then added to the sample tubes to achieve the desired salt concentrations (*i.e.*, 0.1-40 mM). All vials were vortex mixed for about 5 seconds following salt addition to ensure adequate mixing prior to measurements.

**Sedimentation Studies**

Sedimentation of the nanoparticles and clusters was monitored using a UV-VIS-NIR spectrophotometer (Varian Cary 5000). The absorbance of the suspensions at different wavelengths (*i.e.*, 200-1350 nm) were measured at room temperature every 15 seconds for a period of 30-60 minutes. Infiltration of dust and other contaminants in the sample was avoided by prewashing all quartz cuvettes and rinsing with filtered Nanopure® water.

Different concentrations (5-500 mg/L) of magnetite suspension were prepared inside the anaerobic glovebox by diluting the magnetite stock solution and sonicating for about 1-3 minutes. For each suspension of a given mass concentration, 3 mL was transferred to a glass cuvette and capped with a septum stopper. The cuvette was wiped with a non-abrasive, lintless paper prior to placement into the measurement cell. A given volume of 0.1 M NaCl was added to the magnetite suspensions to vary ionic strength and induce sedimentation of the particles.
Baseline corrections were performed prior to sample analysis.

**Magnetite Oxidation**

Magnetite oxidation experiments were performed by transferring 250 mL of deaerated, deionized water to a five neck flask inside the anaerobic glovebox. The flask was sealed with rubber stoppers before taking outside of the glovebox and rested on a Barnstead Electrothermal heating mantle inside a fume hood. The four necks of the flask were then filled with a fritted glass air diffuser, condenser, thermocouple, and stainless steel sampling tube. Moist house air was bubbled through the air diffuser in the side stem of the flask. The condenser occupying the middle neck of the flask was connected to a circulating cold water bath. To adjust the temperature of the suspension inside the flask, the thermocouple was attached to a Cole-Palmer temperature controller regulating the Barnstead electrothermal heating mantle. The flask was wrapped in aluminum foil to maintain the desired temperature of the system.

Once the desired temperature was reached, an aliquot of stock magnetite suspension, pre-sonicated for about one minute, was added to the flask to attain the desired overall mass concentration (i.e., 2 mM). About 3 mL of suspension was sampled from the flask through the sampling tube and transferred to a quartz cuvette for UV-Vis-NIR spectroscopy analysis. Sampling was performed for up to 12 hours depending on the specified temperature of the system. UV-Vis-NIR spectra (200-1350 nm) for each of the samples were obtained using the UV-VIS-NIR spectrophotometer.

Parallel to the spectroscopic analysis, the total Fe and total Fe(II) content for each of the samples obtained at a given time were also evaluated using a modified Ferrozine technique. The Ferrozine reagent was prepared by dissolving 1 g of Ferrozine in 1 L of 50 mM HEPES buffer. The final pH of the reagent was then adjusted to pH 7 by adding NaOH and was stored in an
amber auto-dispenser bottle. To obtain the total Fe(II) concentration of the sample, 1 mL of 0.5 M HCl was added to a given volume of unfiltered aliquot of the sample. After 2 hours, a given volume of the solution was filtered (0.1 μm) into 5 mL of the Ferrozine reagent and the absorbance reading at 562 nm was obtained. The total Fe concentration was obtained using the same procedure, using, however, 1 mL of 11 M HCl and 100 μL of 10% hydroxylamine hydrochloride instead of 0.5 M HCl as the extracting agent. The samples were allowed to digest for 24 hours prior to Ferrozine addition. Standard curves were acquired using Fe(II) stock solution prepared from dissolving ferrous sulfate in a dilution water which was bubbled with nitrogen gas for twenty minutes and whose pH was adjusted to pH 2 using 1 M HNO₃.

Reference
Chapter 3 Effects of Oxidation on the Magnetization of Nanoparticulate Magnetite

Robert L. Rebodos and Peter J. Vikesland

Abstract

Synthetic nanomagnetite has been suggested as a potential reactant for the in-situ treatment of contaminated groundwater. Although the application of magnetite nanoparticles for environmental remediation is promising, a full understanding of particle reactivity has been deterred by the propensity of the nanoparticles to aggregate and become colloidally unstable in the suspension. Attractive magnetic interactions between particles are partially responsible for their aggregation. In this study, we characterized the magnetic behavior of magnetite by determining the saturation magnetization, coercivity, remanent magnetization, susceptibility, and blocking temperature of synthetic magnetite using a superconducting quantum interference device (SQUID). We show how these properties vary in the presence of surface associated solutes such as tetramethylammonium (TMA\(^+\)) and ferrous (Fe\(^{II}\)) cations. More importantly, since magnetite readily reacts with O\(_2\) to produce maghemite, we analyzed the effects of oxidation on the magnetic properties of the particles. Because maghemite has a reported magnetic saturation that is less than that of magnetite, we hypothesized that oxidation would decrease the magnitude of the magnetic attractive force between adjacent particles. The presence of TMA\(^+\) and Fe\(^{II}\) caused a change in the magnetic properties of magnetite potentially due to alterations in its crystalline order. Oxidation of magnetite caused a decrease in saturation magnetization and the anisotrophic barrier between particles resulting in less significant magnetic interactions between particles. Oxidation, therefore, could result in a decrease in the aggregation of magnetite nanoparticles and could enhance its colloidal stability.
1. Introduction

Magnetite nanoparticles are ubiquitous components of the subsurface environment \([1-5]\). In recent years, synthetic nanomagnetite has been suggested as a potential reactant for the in-situ treatment of contaminated groundwater and as an effective ex-situ sorbent of metalloid contaminants due to its high surface area \([6, 7]\). Magnetite exhibits an inverse spinel crystal structure with a unit cell comprised of 32 \(O^2-\) anions, 16 \(Fe^{3+}\) cations, and 8 \(Fe^{2+}\) cations (Figure 3-1a). Half of the \(Fe^{3+}\) ions are tetrahedrally (tet) coordinated, while the other half and all of the \(Fe^{2+}\) are octahedrally (oct) coordinated resulting in a unit cell of \((Fe_8^{3+})_{\text{tet}}(Fe_8^{3+}Fe_8^{2+})_{\text{oct}}O_{32}\). In the octahedral layer, the adjacent positioning of \(Fe^{3+}\) and \(Fe^{2+}\) cations enables electron hopping due to overlap of the d orbitals between iron atoms \([8]\). This activity enables magnetite to have near metallic properties \([9]\).

Magnetite is subject to oxidation because of the reduced iron in the crystalline lattice. In the presence of oxygen \([10, 11]\) magnetite oxidizes to maghemite (\(\gamma\)-\(Fe_2O_3\)):

\[
3 \text{Fe}_3\text{O}_4 + \frac{1}{2} \text{O}_2 + 2 \text{H}^+ \rightarrow 4 \gamma\text{-Fe}_2\text{O}_3 + \text{Fe}^{2+} + \text{H}_2\text{O}
\]

In this process, \(Fe^{2+}_{\text{oct}}\) is oxidized to \(Fe^{3+}_{\text{oct}}\) resulting in vacancies confined to the octahedral sites. Explicitly accounting for these vacancies, the unit cell for maghemite can be written as \((Fe_8^{3+})_{\text{tet}}(Fe_{40/3}^{3+}\Box_{8/3})_{\text{oct}}O_{32}\) where \(\Box\) refers to a vacant site. It has been suggested that an outer coating of maghemite develops at the particle-water interface during magnetite oxidation (Figure 3-1b; ref. 10). To maintain electroneutrality, oxidation proceeds via diffusion of interstitial \(Fe^{2+}\) (or alternatively the simultaneous diffusion of \(Fe^{3+}\) and an electron) to the particle-water interface \([10-12]\). The regenerated \(Fe^{2+}\) surface is then subject to further oxidation. This cycle continues until the particle is completely oxidized.
Because the crystalline structures of magnetite and maghemite are nearly identical, the two oxides have very similar physical properties. Both are considered ferromagnetic, although magnetite has a larger bulk saturation magnetization \( (M_{s,\text{magnetite}} = 92-100 \text{ emu/g}) \) than maghemite \( (M_{s,\text{maghemite}} = 60-80 \text{ emu/g}) \) and a lower Curie temperature \( (T_{c,\text{magnetite}} = 850 \text{ K}; T_{c,\text{maghemite}} = 948 \text{ K}) \) due to antiparallel interactions between the electron spins of tetrahedrally coordinated \( \text{Fe}^{3+} \) and octahedrally coordinated \( \text{Fe}^{3+}/\text{Fe}^{2+} \) \([13, 14]\). Based upon the differences in their respective saturation magnetizations, it is expected that conversion of magnetite into maghemite will affect particle magnetization. Previous studies have suggested that the extent of vacancy ordering following oxidation is dictated by the crystallite size, \( \text{Fe}^{2+} \) content, and impurities \([15]\), which in turn affect the magnetic behavior of the particles.

Although the application of magnetite nanoparticles for environmental remediation is promising \([6, 7]\), a full understanding and characterization of particle reactivity has been deterred by the propensity of the nanoparticles to aggregate and become colloidally unstable. This behavior affects not only nanoparticle transport and delivery, but also potentially their reactivity due to the loss of the specific activity of an individual particle \([16, 1]\). To describe the relative stability or instability of a magnetite suspension, previous studies have used extended Derjaguin, Landau, Verwey, Overbeek (DLVO) theory to evaluate the relative magnitude of the attractive and repulsive forces between particles \([18]\). Classic DLVO theory only considers electrostatic repulsion between the electric double layers of two adjacent particles and attractive Lifshitz-van der Waals forces. This theory has subsequently been extended to incorporate so-called non-DLVO interactions such as short-range repulsive forces of hydration \([19]\). For superparamagnetic particles such as magnetite, it is also necessary to consider magnetic
interactions [20]. Accounting for all four types of interactions, the overall potential energy of interaction, $V_T$, can be defined as

$$V_T = V_{vdW} + V_{ES} + V_{AB} + V_M$$

(2)

where $V_{vdW}$, $V_{ES}$, $V_{AB}$, and $V_M$ are the Lifshitz van der Waals, the electrostatic double layer, the hydration, and the magnetization energies, respectively. In general, positive $V_T$ values are indicative of stable suspensions, while negative $V_T$ values indicate colloidal instability [21-23].

The Lifshitz-van der Waals energy ($V_{vdW}$) can be expressed as

$$V_{vdW} = -\frac{A_{131}}{6} \left( \frac{2a^2}{s(4a+s)} + \frac{2a^2}{(2a+s)^2} + \ln \left( \frac{s(4a+s)}{(2a+s)^2} \right) \right)$$

(3)

where $A_{131}$ is the Hamaker constant for a magnetite (1) surface interacting with a magnetite (1) surface (3), $a$ is the radius of the particle, and $s$ is the distance between the surfaces of two interacting particles. The value of the Hamaker constant can be estimated according to [19]:

$$A_{131} = 24\pi h_0^2 \left( \sqrt{\gamma_{1LW}} - \sqrt{\gamma_{3LW}} \right)^2$$

(4)

where $h_0$ is the minimum equilibrium distance between interfaces (typically assumed to be 0.158 ± 0.008 nm; ref. 19) and $\gamma_{1LW} (= 49.3$ mJ/m$^2$; ref. 18) and $\gamma_{3LW} (= 21.8$ mJ/m$^2$; ref. 19) are the Lifshitz–van der Waals components of the surface free energies of magnetite and water, respectively. Using equation 4, $A$ was estimated to be $1.04 \times 10^{-20}$ (Nm). This value is only a factor of 5 lower than the value of $5 \times 10^{-20}$ Nm used by Tsouris and Scott [24] and Chin et al. [25] for magnetite. However, it is an order of magnitude smaller than the value of $10^{-19}$ Nm used by Phenrat et al. [23]. In the results and discussion, we examine the implications of the variability of these Hamaker constants on the calculated interaction energy $V_T$. 

3-4
The electrostatic double layer potential energy ($V_{ES}$) is defined as:

$$V_{ES} = 2\pi \varepsilon_0 \varepsilon_r \phi_0^2 \ln \left(1 + e^{-ks} \right) \tag{5}$$

where $\phi_0$ is the surface potential ($= -1.3$ mV; ref. 26), $\varepsilon_0$ is the permittivity of the vacuum ($= 8.85 \times 10^{-12}$ Fm), $\varepsilon_r$ is the relative dielectric constant for water ($= 78.5$ at 298 K), and $\kappa$ is the inverse Debye length:

$$\kappa = \sqrt[4]{\frac{2N_A e^2 \sum c_i z_i^2}{e \varepsilon_0 \varepsilon_r \kappa B T}} \tag{6}$$

where $c_i$ and $z_i$ are the concentration and valence of ion $i$, respectively, $N_A$ is Avogadro’s number, $e$ is the elementary charge ($= 1.602 \times 10^{-19}$ coulombs), $k_B$ is the Boltzmann constant ($= 1.381 \times 10^{-23}$ J/K), and $T$ is the temperature in Kelvin.

For an amphoteric oxide such as magnetite, there is a repulsive interaction that should also be accounted for due to water hydration of the particle surface [27]. For particles to associate with one another, this hydration layer must be breached, resulting in a repulsive energy [19]. This repulsive energy has been defined as:

$$V_{AB} = V_{AB}(h_0) \pi a \lambda e^\frac{h_0 - s}{\lambda} \tag{7}$$

where $\lambda$ is the water correlation distance. Typically a value of $\lambda = 1$nm is assumed for hydrophilic particles in water [19, 2]. $V_{AB}(h_0)$ is the acid-base interfacial energy at the equilibrium distance $h_0$ and is defined as:

$$V_{AB}(h_b) = -4 \left( \sqrt[4]{\gamma_1^+ \gamma_1^-} + \sqrt[4]{\gamma_3^+ \gamma_3^-} - \sqrt[4]{\gamma_1^+ \gamma_3^-} - \sqrt[4]{\gamma_1^- \gamma_3^+} \right) \tag{8}$$
where $\gamma^+$ and $\gamma^-$ are the electron donor and acceptor parameters of the surface tension of magnetite ($\gamma^+ = 0.17 \text{ mJ/m}^2; \gamma^- = 55.4 \text{ mJ/m}^2; \text{Ref: 18}$) and water ($\gamma^+_3 = \gamma^-_3 = 25.5 \text{ mJ/m}^2; \text{ref. 19}$).

Young and Prieve [20] have shown that magnetic particle alignment in the magnetic field of the Earth can occur even for superparamagnetic particles. Accordingly, it is necessary to estimate the magnetic attractive forces that can occur between individual magnetite nanoparticles. Although the exact magnitude of the magnetic attractive force is difficult to determine due to variability in particle-particle positioning and actual spin alignment, an upper bound on the magnetic attraction can be calculated by assuming that the spins for two interacting particles align in a head to tail fashion [26]:

$$V_m = -\frac{8\pi \mu_0 a^3 m_s^2}{9 \left( \frac{s}{a} + 2 \right)^3}$$  \hspace{1cm} (9)

where $m_s$ is the saturation magnetization of a given nanoparticle. As noted previously, bulk saturation magnetization values for magnetite are generally higher than those for maghemite [29]. These values, however, are sensitive to the particle size [13] such that estimates based on bulk $M_s$ values generally overestimate the magnitude of the magnetic attraction. Since magnetic attractive forces can destabilize otherwise stable suspensions, the magnitude of this destabilization is a function of the particle size and the saturation magnetization. Because the saturation magnetization of magnetite is higher than that of maghemite, a change in the particle oxidation state should also affect particle stability. Recently, Roca et al. [30] illustrated that a small change in oxidation state resulted in a decrease in $m_s$ of 5-10%.
As mentioned previously, magnetite readily reacts with O\textsubscript{2} to produce maghemite. Because maghemite has a reported magnetic saturation that is less than that of magnetite we hypothesized that oxidation would decrease the magnitude of the magnetic attractive force between adjacent particles. As such, oxidation might be expected to enhance the colloidal stability of the suspension. In this study, we determined the saturation magnetization, coercivity, remanent magnetization, susceptibility, and blocking temperature of synthetic magnetite using a superconducting quantum interference device (SQuID). As documented herein, the oxidation of magnetite results in a decreased saturation magnetization and thus an expected decrease in the aggregation of magnetite nanoparticles. We analyze the impacts of the decreased magnetization using extended DLVO theory.

2. Experimental Section

**General.** All experimental solutions were prepared using de-aerated, deionized water (> 18.1 MΩ). Water was de-aerated by boiling for 30 minutes and then sparging with either argon or nitrogen gas for at least 30 minutes while boiling continued. De-aerated water was removed from the heating source, capped, and transferred to the anaerobic chamber. Reagent grade chemicals were used without further purification in all experiments.

**Magnetite synthesis.** Magnetite nanoparticles were synthesized using a co-precipitation method adapted from Vayssieres, et al. [31]. In brief, a mixture of 0.1 M FeCl\textsubscript{2} and 0.2 M FeCl\textsubscript{3} was added drop-wise (~1 drop/s) to a well-mixed solution of 1 M NaOH and 1 M NaCl. The final ratio of iron solution to base solution was kept at 3:2 to maintain the pH above 12. Polypropylene containers were used to avoid silicate leaching from glass vessels under the high pH synthesis conditions. Excess salts were removed by magnetically separating the precipitated nanoparticles and by rinsing with argon-purged, deionized water until the pH of the supernatant
was in the 7-8.5 range. Tetramethylammonium hydroxide (TMAOH) functionalized nanoparticles were synthesized using the same co-precipitation method except 1 M TMAOH was used instead of 1 M NaOH. The bulky tetramethylammonium (TMA⁺) cations are expected to sterically stabilize the suspension relative to NaOH [32] Prepared magnetite stocks were stored in the anaerobic glovebox for periods up to 2 months. The mass concentration of a magnetite stock was gravimetrically determined in triplicate by drying 2 mL of slurry in a 75 °C oven. The final mass of dried sample was converted into an equivalent magnetite mass using the Fe₃O₄/γ-Fe₂O₃ gravimetric ratio and assuming 100% conversion of Fe₃O₄ into γ-Fe₂O₃. The magnetite suspensions agglomerate during storage and thus rigorous mixing and brief sonication (t < 1 minute) of the stock suspension was required to breakup agglomerates and to re-suspend the particles prior to sampling.

**Particle Characterization.** The morphology, size, and electron diffraction patterns of nanoparticulate magnetite were characterized using a Philips 420T TEM at 100 keV. Particle slurries were mounted on carbon coated TEM grids and dried in an aerobic environment for a minimum of 48 hours. Collected images were digitally transferred using a slow scan 3086 × 2056 pixel camera. Dried powder samples of nanoparticulate magnetite were characterized by XRD using a Rigaku RAPID Curved IP X-ray powder diffractometer with Cu Kα radiation and an image plate detector. Infrared and confocal Raman spectra of the dried magnetite samples were obtained using a Midac M2004 ATR FT-IR spectrometer with a diamond prism and a WITec alpha500R confocal Raman/AFM, respectively.

**Magnetic Characterization.** The magnetic characteristics of magnetite were assessed using a 7-T Quantum Design MPMS SQUID magnetometer. Dried samples were packed into gelatin capsules between cotton plugs. Zero field cooled-field cooled (ZFC-FC) loops were obtained
from 5-300 K. In the ZFC portion of the loop, the nanoparticles were cooled in the absence of an applied field to 5 K. A magnetic field of 0.5 kOe was then applied as the temperature was increased to 300 K. In the FC portion of the loop, the temperature is decreased from 300 K to 5 K in the presence of the 0.5 kOe field. Hysteresis loops of dried samples were performed in fields up to ±70 kOe at 5 K and 298 K.

To evaluate how co-solutes affect the magnetization of magnetite, we conducted experiments wherein either 0.1 M NaCl or 0.1 M FeCl₂ was added to a 1 mM NaOH-magnetite suspension with a pH of 8. NaCl was used as an inert electrolyte, while Fe²⁺ was used as a redox active co-solute that can affect the magnetite oxidation state [33]. Herein we follow the nomenclature of Gorski and Scherer [33] and use Arabic superscripts to indicate structural metal species and Roman superscripts for dissolved or sorbed species. One sample of each suspension was taken immediately after their production and a second was taken after a 24 hour anaerobic equilibration period. These samples were dried in the anaerobic chamber and then tested via SQUID.

Oxidation experiments employing TMAOH-magnetite were performed by transferring 250 mL of deaerated, deionized water to a five neck round bottom flask inside the anaerobic glovebox. The flask was then sealed prior to removing it from the glovebox. Once removed from the glovebox, the flask was set upon a Barnstead Electrothermal heating mantle in a fume hood. The four necks of the flask were then fitted with a glass diffuser rod, condenser, thermocouple and stainless steel sampling tube (Supporting Information Figure 3-S1). Moist house air was bubbled through the air diffuser in the side stem of the flask. The condenser occupying the middle neck of the flask was connected to a circulating cold water bath. To adjust the temperature of the suspension inside the flask, the thermocouple was attached to a Cole-Palmer Temperature
Controller regulating the heating mantle. To maintain the desired temperature of 84 °C, the flask was wrapped in aluminum foil.

Once the water temperature in the flask reached 84 °C, a given amount of the stock magnetite suspension, pre-sonicated for about one minute, was added to attain a 2 mM mass concentration (pH = 7.5). Immediately after adding the stock, an initial sample of ≈ 3 mL was removed via the sampling tube and transferred to the anaerobic glovebox. The sample was then dried and analyzed via SQUID. A parallel experiment with NaOH-magnetite was conducted by heating it at ≈75 °C for 12 hours.

The total Fe and total Fe$^{2+}$ content of each of the samples were determined using a modified Ferrozine technique. Ferrozine reagent was prepared by dissolving 1 g of Ferrozine (benzenesulfonic acid, 4,4'[3-(2-pyridinyl)-1,2,4-triazine-5,6-diyl]bis-, monosodium salt) in 1 L of 50 mM HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid, purity >99%) buffer. The final pH of the reagent was then adjusted to pH 7 by adding NaOH. The prepared solution was stored in an amber auto-dispenser bottle. To obtain the total Fe$^{2+}$ content of the sample, 1 mL of 0.5 M HCl was added to an unfiltered sample aliquot. After 2 hours, a given volume of the solution was filtered (0.1 mm) into 5 mL of Ferrozine reagent and the absorbance at 562 nm was obtained. Total Fe was determined using the same procedure; however, 1 mL of 11 M HCl and 100 mL of 10% hydroxylamine hydrochloride were used instead of 0.5 M HCl. Total Fe samples were digested for 24 hours prior to Ferrozine addition. Standard curves were acquired using Fe$^{II}$ stock solutions prepared by dissolving ferrous sulfate in a dilution water which had been bubbled with nitrogen gas for twenty minutes and whose pH was adjusted to pH 2 using 1 M HNO$_3$.  

3-10
3. Results and Discussion

**Particle characterization.** Magnetite nanoparticles produced in NaOH (referred to hereafter as NaOH-magnetite) or in TMAOH (TMAOH-magnetite) were generally cubospherical (Figure 3-2), as expected for particles produced via coprecipitation [13, 34]. Scion Image (Scion Corporation) was used to determine median particle sizes from the collected TEM images. Based upon a log-normal distribution, the median TEM diameter ($d_{\text{TEM}}$) for NaOH-magnetite ($n=265$) was determined to be 10.0 nm (polydispersity $P = \text{standard deviation/mean} = 0.15$), while TMAOH-magnetite ($n=300$) was smaller with a median diameter of 7.93 nm ($P=0.085$). The difference in the size of the nanoparticles synthesized using the two approaches is most likely the result of an alteration in the growth mechanism of the particles dictated by the identity of the base. As shown by the FT-IR spectra for TMAOH-magnetite (Figure 3-S2), TMA$^+$ cations are associated with the surface of TMAOH-magnetite. This association limits the growth of a nascent nanoparticle and facilitates the colloidal stability of the nanoparticles via steric interactions.

X-ray diffraction patterns for NaOH-magnetite and TMAOH-magnetite are consistent with those for magnetite/maghemite (Figure 3-S3a). Magnetite and maghemite have similar XRD patterns and it is difficult to differentiate the two phases by XRD [9]. Furthermore, because the samples for XRD analysis were air-dried, the particles should consist of a mixture of magnetite and maghemite. The diffractogram for TMAOH-magnetite exhibits significant line broadening relative to NaOH-magnetite. This broadening reflects the smaller size of the TMAOH-magnetite particles and is a result of the lower periodicity of the smaller crystals [35]. Plots of $B \cos \theta$ vs. $\sin \theta$ (where $B$ is the full width half maximum) for both NaOH-magnetite and TMAOH-magnetite (Figure 3-S3b) are essentially horizontal indicating that the broadening is the result of
size effects (36). Applying the Scherer formula [6] to the 311 peak, the XRD diameter ($d_{XRD}$) for NaOH-magnetite was determined to be 12.4 nm, while that for TMAOH-magnetite was 9.14 nm. These $d_{XRD}$ values should be considered volume average sizes with a level of accuracy of $\approx 25\%$ [36]. As such, quantitative comparison with the $d_{TEM}$ values is not viable, nonetheless the relative magnitudes of the values determined for NaOH-magnetite and TMAOH-magnetite follow the same trend.

FT-IR spectra (Figure 3-S2) for NaOH-magnetite and TMAOH-magnetite exhibit absorption bands at 667, 1087, and 1620 cm$^{-1}$ typical of natural and synthetic magnetites [37]. The spectrum for TMAOH-magnetite differs from that of NaOH-magnetite due to absorption bands at 948, 1320, and $\sim 1500$ cm$^{-1}$. These bands are consistent with the adsorption of TMA$^+$ at the nanoparticle surface [38] (Figure 3-S2). Similar to the FT-IR spectra, Raman spectra for NaOH-magnetite and TMAOH-magnetite (Figure 3-S4) are consistent with magnetite-maghemite. These spectra exhibit a broad-Raman band centered at approximately 680 cm$^{-1}$ typically attributed to magnetite [3, 39]. However, the full-width half maximum of $\approx 100$ cm$^{-1}$ for this band exceeds that of magnetite alone [3] and is indicative of the presence of both magnetite and maghemite in the dried samples [40].

**Magnetic properties.** Magnetization curves obtained in ZFC and FC modes for NaOH-magnetite and TMAOH-magnetite are shown in Figure 3-3. These curves show that the blocking temperature ($T_B$), or the temperature at which there is a maximum in the ZFC curve, is much higher for NaOH-magnetite ($T_B = 290 \pm 5$ K) than for TMAOH-magnetite ($T_B = 85 \pm 2$ K). At $T_B$, magnetization is maximized because there is enough thermal energy to enable individual nanoparticles to align with the magnetic field. For temperatures above $T_B$ the thermal energy is large enough to enable the particles to overcome the field alignment, thus leading to decreased
magnetization. The lower \( T_B \) for TMAOH-magnetite shows that less thermal energy is necessary to overcome the field alignment relative to NaOH-magnetite. This observation suggests that dipolar interactions occur more extensively between the NaOH-magnetite particles than between the TMAOH-magnetite particles and that NaOH-magnetite is more aggregated and has a higher anisotropy energy [41-43]. This conclusion is supported by the slight kink in the ZFC curve for NaOH-magnetite at 35 K that may reflect a Verwey transition \((T_V)\). Verwey transitions generally occur for bigger particles or for aggregated systems. For bulk magnetite \( T_V \) is reported to be \( \approx 120 \) K, while for nonaggregated nanoparticulate magnetite it is lower or nonexistent [13].

Mathematically \( T_B \) can be defined as follows [29]:

\[
T_B = \frac{kV}{2k_B}
\]

where \( k \) is the magnetic anisotropy constant for magnetite \((1.4 - 5 \times 10^4 \text{ J/m}^3)\); refs. 9, 44), \( V \) is the nanoparticle volume, and \( k_B \) is the Boltzmann constant. Using this reported range of anisotropy values and assuming spherical particles with diameters of either 10.0 (NaOH-magnetite) or 7.96 nm (TMAOH-magnetite), \( T_B \) was estimated to range between 21.2-75.8 K and 10.7-38.2 K, respectively. The fact that our experimentally determined values of \( T_B \) are higher than the calculated values for both samples suggests that magnetic interparticle interactions occur not only for NaOH-magnetite, but also for TMAOH-magnetite [42]. The relative magnitude of these interactions is larger for NaOH-magnetite, but still significant for TMAOH-magnetite.

Hysteresis loops for NaOH-magnetite and TMAOH-magnetite were obtained at 298 and 5 K and are shown in Figures 3-4 and 3-S5, respectively. For both NaOH-magnetite and TMAOH-magnetite, the measured magnetization was dependent on the magnitude of the applied field, but not on the sign of the field. The reversibility and symmetry of the curves at both temperatures
reflect the superparamagnetic like-behavior of both types of particles [13, 45]. This observation is consistent with the fact that both materials have diameters well below the 26 nm cutoff estimated for magnetite to exhibit superparamagnetic behavior [46]. Although the ZFC-FC curves established that both NaOH-magnetite and TMAOH-magnetite exhibit some magnetic coupling between adjacent nanoparticles, the coupling was insufficient to make the curves antisymmetric as would be expected for highly coupled magnetic phases [13, 4].

The saturation magnetization ($m_s$), initial magnetic susceptibility ($\chi_{\text{ini}}$), coercivity ($H_c$), and magnetic remanence ($m_r$) generally define the magnetic characteristics of a material and were determined via graphical analysis of the collected hysteresis loops. $m_s$ was obtained via extrapolation of the measured magnetization loops to infinite field, $\chi_{\text{ini}}$ is the slope of the magnetization curve at low field, $H_c$ is the field strength required to demagnetize the sample after it has been magnetically saturated, and $m_r$ is the magnetism of the particles in the absence of an applied field. As summarized in Table 3-1, NaOH-magnetite exhibits higher $m_s$, $m_r$, and $\chi_{\text{ini}}$ values at both 5 and 298 K than TMAOH-magnetite, while the $H_c$ values are statistically indistinguishable for the two samples.

At room temperature, the $m_s$ values for both magnetite samples are lower than the $M_s$ of bulk magnetite (=92-100 emu/g; ref. 29), but are similar to the $m_s$ values previously reported for magnetite nanoparticles of similar sizes and surface functionalization ($m_s = 60.1-67.9$ for $\approx$10 nm particles; Refs. 13, 29, 47, 48). A decrease in magnetic susceptibility with particle size has previously been observed [49] and can be attributed to spin disorder at the particle surface caused by surface inhomogeneities and truncation of the crystalline lattice [13, 49, 50]. The lower $m_s$ for TMAOH-magnetite relative to NaOH-magnetite may be the combined result of its smaller particle size as well as the association of TMA$^+$ cations at the particle surface. It was
recently shown [34] that the TMA$^+$ cations at the particle surface produce a layer of partially-oxidized, non-stoichiometric magnetite/maghemite that surrounds the crystal core. The existence of this non-magnetic shell would also lead to a decreased $m_s$.

At 298 K, the $H_c$ and $m_r$ values are low (< 25 Oe and < 2 emu/g, respectively) for both NaOH-magnetite and TMAOH-magnetite. The non-zero values for these parameters indicate that the particles exhibit ferrimagnetism indicative of interparticle interactions at room temperature [34, 43]. However, this ferromagnetic effect is relatively small given that the coercivity of ferromagnetic bulk magnetite ranges from 115-400 Oe [9]. Because of its smaller particle size, we anticipated TMAOH-magnetite would have a lower coercivity than NaOH-magnetite since $H_C$ generally decreases with particle size [13]. However, the presence of the TMA$^+$ cations at the nanoparticle surface apparently increased the surface anisotropy to such a degree that $H_c$ for TMAOH-magnetite is larger than it would have been without the surface functionalization. A similar effect on $H_c$ has previously been observed with adsorbed surfactants [29, 51].

The initial magnetic susceptibility ($\chi_{ini}$) reflects the magnitude of the effective anisotropy barrier (i.e., its resistance to magnetization directionalization) of a material. A larger $\chi_{ini}$ value indicates particles that more easily interact magnetically. Comparing their relative $\chi_{ini}$ values again reveals the greater level of interparticle interactions that occur between the NaOH-magnetite grains relative to TMAOH-magnetite. To further evaluate the relative anisotropy of these materials we used the experimentally determined $H_c$ and $m_s$ values obtained at 5 K to calculate the effective anisotropy ($k_{eff}$) using the relation:

$$k_{eff} = \frac{H_c m_s}{2}$$  \hspace{1cm} (11)
Based upon this equation, we obtained $k_{\text{eff}}$ values of 8220 and 7030 J/m$^3$ for NaOH-magnetite and TMAOH-magnetite, respectively. These values are smaller than the anisotropy constant for bulk magnetite ($k$), but $\approx 2\times$ larger than those for magnetite nanoparticles that are less strongly magnetically coupled [13].

The FTIR results clearly demonstrate that TMA$^{+}$ cations are present at the TMAOH-magnetite surface and in parallel studies we have found that this surface functionalization enhances the colloidal stability of these particles relative to NaOH-magnetite (Chapter 4). However, magnetic characterization indicates that TMAOH-magnetite remains subject to interparticle magnetic interactions as shown by its high $\chi_{\text{ini}}$ and higher than anticipated $T_B$. Similarly, evaluation of the $m_r/m_s$ ratio at 5 K, which should be $> 0.5$ for non-interacting, randomly oriented particles with uniaxial symmetry [13], indicates a value of 0.26 or less. The decrease in the $m_r/m_s$ ratio is consistent with magnetic interactions between the particles [43]. For TMAOH-magnetite this result indicates that although the TMA$^{+}$ cations associate with the surface that their presence is not sufficient to entirely diminish interparticle interactions.

**Magnetic particle size.** For superparamagnetic-like particles such as those being studied here it is possible to calculate an apparent magnetic diameter ($d_{\text{mag}}$) for each particle using the approach of Chantrell et al. [52].

$$d_{\text{mag}} = \left[ \frac{18k_B T}{\pi m_s} \frac{\chi_{\text{ini}}}{M_s} \frac{1}{H_0} \right]^{1/3}$$

(12)

where $1/H_0$ is defined as ($\approx (\Delta M/\Delta(1/H))_{M\rightarrow 0}$; with $M$ the applied magnetization) and $M_s$ is the saturation magnetization of bulk magnetite ($= 95$ emu/g). Using these parameters, we estimated the $d_{\text{mag}}$ values for NaOH-magnetite and TMAOH-magnetite to be 5.5 and 4.1 nm, respectively. In each case, the calculated values are $\approx 50\%$ of the physical particle diameter obtained via
analysis of the TEM data. This result indicates that each particle consists of a highly magnetic core surrounded by a shell of less magnetic or nonmagnetic material. Past studies conducted with magnetite produced by coprecipitation have obtained similar results [13]. Only when magnetite is produced by thermal decomposition do you generally get $d_{\text{mag}}$ values that approach those of the physical size [30].

**Effect of Fe$^{II}$.** Past studies have shown that the sorption of Fe$^{II}$ to the magnetite surface results in the transfer of an electron from sorbed Fe$^{II}$ to the nanoparticle lattice resulting in production of surface Fe$^{III}$ and interstitial Fe$^{2+}$ [10, 33]. To examine how this electron transfer affects magnetite magnetization we obtained magnetization curves for Fe$^{II}$ treated NaOH-magnetite and compared them with those of NaOH-magnetite alone.

Addition of Fe$^{II}$ led to a statistically significant decrease in $m_s$ and an increase in $m_r$, but insignificant changes in $H_c$ and $\chi_{\text{init}}$ for NaOH-magnetite (Table 3-2). This result suggests that the incorporation of Fe$^{II}$ within the crystalline lattice disrupts the crystalline order leading to decreased magnetism. Comparison of 24-hour aged versus un-aged samples indicates this effect occurs quite rapidly. Additional studies examining Fe$^{II}$ incorporation that employ both stoichiometric and non-stoichiometric magnetite [33] would provide additional insights about this interesting behavior. Such studies were beyond the scope of the present investigation.

**Effect of oxidation on $m_s$.** Particle oxidation results in a decrease in $m_s$ for both NaOH-magnetite and TMAOH-magnetite (Figures 3-5 and 3-S6; Table 3-2). These decreases are consistent with the conversion of magnetite into maghemite (documented via both FT-IR, Figure 3-S2; and Raman spectroscopy, Figure 3-S4), which has a lower saturation magnetization owing to its smaller magnetic moment (2.3$\mu_B$ for maghemite versus 4.1$\mu_B$ for magnetite; ref. 53).
Oxidation of NaOH-magnetite led to statistically significant declines in $m_r$ and $\chi_{\text{ini}}$ and an increase, albeit statistically insignificant, in $H_c$ at 5 K and a decrease in this parameter at 298 K. Based upon past studies we had expected the decline in $m_s$, but also anticipated that $H_c$ would increase. Previously Ong et al. [54] measured a decrease in $m_s$ from 45 emu/g to 10 emu/g upon thermal oxidation of 10 nm magnetite at 675 °C. Under our milder experimental conditions we would not expect such a marked change in $m_s$. The observed decrease in $\chi_{\text{ini}}$ suggests that particle oxidation decreases the anisotropic barrier and results in less significant magnetic interactions between particles. Given that NaOH-magnetite was initially highly coupled magnetically the change in this parameter was quite large.

For TMAOH-magnetite, which did not exhibit the same extent of magnetic coupling, the effects of oxidation were subtler than for NaOH-magnetite. $m_s$ at 298 K declined from 62.2 (± 0.266) to 58.0 (± 0.352) emu/g over the four hour oxidation period at 84 °C. At the same time, $\chi_{\text{ini}}$ decreased from 0.049 (± 0.0043) to 0.044 (± 0.0036) emu/g/Oe. Interestingly, neither $m_r$ nor $H_c$ was sensitive to oxidation. This latter observation indicates that oxidation does not alter the ability of these particles to retain their magnetism at low field.

During the four-hour oxidation period the total Fe$^{II}$ content of the nanoparticles decreases 4× from 21.6 to 5.1%. Stoichiometric magnetite has a Fe$^{II}$ content of 33.3% and thus our magnetite had oxidized during storage prior to its use in these experiments. Gorski and Scherer recently observed similar oxidation when magnetite is stored in aqueous solutions at circumneutral pH [33]. As introduced previously, the conversion of magnetite into maghemite has been proposed to occur via the development of a core-shell intermediate [6, 10]. Past studies have shown that the overall saturation magnetization ($m_s$) for composite particles consisting of a core with
saturation magnetization \( m_{s1} \) and a shell with saturation magnetization \( m_{s2} \) can be described by [55, 56]:

\[
m_s = \frac{m_{s1} V_1 + m_{s2} V_2}{V_1 + V_2}
\]

where \( V_1 \) and \( V_2 \) are the volumes of the core and shell, respectively. Assuming a spherical geometry, we solved equation 13 to consider a case where the core size changes over time:

\[
m_s = \frac{m_{s1} R_{core}^3 + m_{s2} R_{total}^3 - m_{s2} R_{core}^3}{R_{total}^3}
\]

where \( R_{total} \) and \( R_{core} \) are the radius of the particle and the radius of the core, respectively. The difference between the two radii corresponds to the thickness of the shell, \( t \). Using the collected \( m_s \) vs. \%Fe\(^{II}\) data we estimated the values for \( m_{s1} \) (\%Fe\(^{II}\) = 0.33 for stoichiometric magnetite) and \( m_{s2} \) (\%Fe\(^{II}\) = 0.00 for stoichiometric maghemite) to be 62.6 and 51.9 emu/g by linear extrapolation of the upper and the lower portions of this curve, respectively (Figure 3-6a). Using these values we estimate that for a TMAOH-magnetite particle with a \( d_{TEM} \) of 7.92 nm that the width of the maghemite shell increases from 0.086 nm initially to 0.73 nm after four hours (Figure 3-6b). These estimates result in a much larger magnetite core than was estimated via equation 12. The disparity between the two calculations may reflect the fact that equation 14 assumes the presence of two distinct phases – a magnetite core and a maghemite shell. As recently discussed in the literature [33] it is not clear that such a clear delineation actually occurs since solid solutions of magnetite/maghemite are possible. Experiments utilizing stoichiometric magnetite as a starting material in place of our partially oxidized magnetite will serve to better determine if equation 14 accurately defines the magnetism of this system.

**Implications to magnetite colloidal stability.** To examine the effects of changes in magnetization on colloidal stability we calculated potential energy profiles for nanoparticles with
$m_s$ values varying from 62.6 to 51.9 emu/g. This range corresponds to that expected for the conversion of stoichiometric magnetite into stoichiometric maghemite due to oxidation. For these calculations we assume that oxidation does not alter either the Hamaker constant or the surface potential of the particles significantly. As shown in Figure 3-7a, particle oxidation results in a decrease in the potential energy associated to the magnetic forces such that at a separation distance of 5 nm fully oxidized particles experience a 31% lower attraction than unoxidized particles (-0.2606 $k_B T$ versus -0.3791 $k_B T$).

The implications of the oxidation-induced decrease in the magnetic force on the overall potential energy profile were evaluated both in the absence (Figure 3-7b) and in the presence of repulsive hydration forces (Figure 3-S7). The potential energy curves considering magnetic forces as well as attractive van der Waals-Lifshitz forces and electrostatic repulsion illustrate that oxidation increases the magnitude of the repulsive energy barrier, thereby suggesting that oxidation should moderately enhance colloidal stability. In contrast, upon consideration of hydrophobic forces the potential energy curves indicate that particle oxidation should not dramatically alter the colloidal stability. This latter result is due to the magnitude of the short-range repulsive hydrophobic force ($\approx 73 \, k_B T$ at 1 nm separation) that completely swamps out the effects of the other forces. Given that magnetite nanoparticle suspensions can be readily aggregated it seems unlikely that a hydrophobic force of this magnitude actually exists. The inclusion or exclusion of terms attempting to account for hydrophobic forces in extended DLVO calculations is an area of ongoing research beyond the scope of the present study.

4. Conclusions

In this study, magnetite nanoparticles synthesized in the presence of either NaOH or TMAOH were tested with respect to their magnetic properties. Based upon their corresponding ZFC-FC
curves and the blocking temperature derived from them, the relative magnitude of dipolar interactions between NAOH-magnetite is larger than that for the TMAOH-magnetite nanoparticles. Based upon their magnetic hysteresis loops, however, both magnetite nanoparticles exhibited superparamagnetic-like behavior which is expected for particles within this size range. Although the ZFC-FC indicated magnetic coupling between particles, this coupling was insufficient to make the hysteresis curves antisymmetric. The observed lower saturation magnetization and higher surface anisotropy for TMAOH-magnetite relative to NaOH-magnetite may be due to its smaller particle size and the presence of TMA$^+$ cations at the surface.

The effect of oxidation on magnetization was studied by performing kinetic studies on both particle types. The observed decline in saturation magnetization for both NaOH-magnetite and TMAOH-magnetite after oxidation was consistent with the transformation of magnetite to maghemite. Oxidation caused a decrease in the anisotropic barrier resulting in less significant magnetic interactions between particles. This effect is more pronounced for NaOH-magnetite, which was more coupled magnetically than TMAOH-magnetite prior to oxidation. For TMAOH-magnetite, remanent magnetization and magnetic susceptibility were insensitive to oxidation implying that for these particles, their magnetism at low field is retained following oxidation.

References


Table 3-1. Particle diameters and magnetization parameters for NaOH-magnetite and TMAOH-magnetite. $d_{\text{TEM}}$ determined via analysis of TEM images, $d_{\text{XRD}}$ determined via Scherer analysis. Saturation magnetization ($m_s$), remanent magnetization ($m_r$), coercivity ($H_c$), and initial susceptibility ($\chi_{\text{ini}}$) determined via graphical analysis of collected magnetization curves at 298 and 5 K. Reported errors are the standard error obtained by analysis of the rising and falling magnetization curves.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Temp. (K)</th>
<th>$m_s$ (emu/g)</th>
<th>$m_r$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
<th>$\chi_{\text{ini}}$ (emu/g/Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH-mag</td>
<td>298</td>
<td>79.9 ± 0.205</td>
<td>1.91 ± 0.221</td>
<td>23 ± 3.2</td>
<td>0.082 ± 0.0017</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>93.4 ± 0.112</td>
<td>23.9 ± 0.160</td>
<td>356 ± 52</td>
<td>0.068 ± 0.0096</td>
</tr>
<tr>
<td>TMAOH-mag</td>
<td>298</td>
<td>62.2 ± 0.266</td>
<td>1.11 ± 0.209</td>
<td>23 ± 6.2</td>
<td>0.049 ± 0.0043</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>73.6 ± 0.478</td>
<td>15.7 ± 0.113</td>
<td>386 ± 35</td>
<td>0.041 ± 0.0038</td>
</tr>
</tbody>
</table>
Table 3-2. Effects of co-solutes and particle oxidation on the magnetic properties of NaOH-magnetite and TMAOH-magnetite.

<table>
<thead>
<tr>
<th></th>
<th>Temp.</th>
<th>$m_s$ (emu/g)</th>
<th>$M_r$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
<th>$\chi_{ini}$ (emu/g/Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxidation experiments</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH-mag</td>
<td>298</td>
<td>79.9 ± 0.205</td>
<td>1.91 ± 0.221</td>
<td>23 ± 3.2</td>
<td>0.082 ± 0.0017</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>93.4 ± 0.112</td>
<td>23.9 ± 0.160</td>
<td>356 ± 52</td>
<td>0.068 ± 0.0096</td>
</tr>
<tr>
<td>Oxidized NaOH-magnetite</td>
<td>298</td>
<td>75.1 ± 0.123</td>
<td>0.54 ± 0.049</td>
<td>7 ± 0.9</td>
<td>0.073 ± 0.0028</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>79.9 ± 3.18</td>
<td>15.5 ± 0.086</td>
<td>430 ± 73</td>
<td>0.037 ± 0.0063</td>
</tr>
<tr>
<td>TMAOH-magnetite oxidation time = 0 hrs</td>
<td>298</td>
<td>62.2 ± 0.266</td>
<td>1.11 ± 0.209</td>
<td>23 ± 6.2</td>
<td>0.049 ± 0.0043</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>73.6 ± 0.478</td>
<td>15.7 ± 0.113</td>
<td>390 ± 35</td>
<td>0.041 ± 0.0038</td>
</tr>
<tr>
<td>TMAOH-magnetite oxidation time = 1 hrs</td>
<td>298</td>
<td>62.0 ± 0.320</td>
<td>1.02 ± 0.127</td>
<td>23 ± 4.7</td>
<td>0.045 ± 0.0038</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>75.1 ± 0.310</td>
<td>17.2 ± 0.088</td>
<td>390 ± 80</td>
<td>0.045 ± 0.0095</td>
</tr>
<tr>
<td>TMAOH-magnetite oxidation time = 2.5 hrs</td>
<td>298</td>
<td>61.7 ± 0.307</td>
<td>1.03 ± 0.126</td>
<td>23 ± 4.5</td>
<td>0.046 ± 0.0037</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>75.7 ± 0.277</td>
<td>16.7 ± 0.017</td>
<td>430 ± 48</td>
<td>0.039 ± 0.0043</td>
</tr>
<tr>
<td>TMAOH-magnetite oxidation time = 4 hrs</td>
<td>298</td>
<td>58.0 ± 0.352</td>
<td>0.99 ± 0.124</td>
<td>23 ± 4.7</td>
<td>0.044 ± 0.0036</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>73.7 ± 0.398</td>
<td>15.7 ± 0.114</td>
<td>390 ± 36</td>
<td>0.041 ± 0.0038</td>
</tr>
</tbody>
</table>
Figure 3-1. A) Inverse spinel crystal structure of magnetite and maghemite. B) The oxidation of magnetite to maghemite occurs via diffusion of Fe$^{II}$ from the particle core towards the nanoparticle surface.
Figure 3-2. TEM images and particle size distributions for NaOH-magnetite (A,B) and TMAOH-magnetite (C,D).
Figure 3-3. ZFC-FC curves for NaOH-magnetite and TMAOH-magnetite acquired using an applied field of 500 Oe.
Figure 3-4. Hysteresis loops acquired at 298 K for NaOH-magnetite and TMAOH-magnetite.
Figure 3-5. Magnetization curves at 298 K for magnetite (TMAOH) aerated at 84.4 °C for 4 hours. The inset illustrates the coercivity field $H_C$ and remanent magnetization $M_R$. 
Figure 3-6. A) Decrease in saturation magnetization $m_s$ (emu/g) as a function of the change in %Fe$^{2+}$ content. B) Relationship between the saturation magnetization, $m_s$ (emu/g) and the thickness of the shell based on the %Fe$^{2+}$ curves.
Figure 3-7.  A) Effects of oxidation on the magnetic interaction energy for a pair of 10 nm magnetite nanoparticles. $M_s$ was varied from 62.6 to 51.9 emu/g, this range corresponds to the change expected for the conversion of stoichiometric magnetite into stoichiometric maghemite. B) Potential energy profiles calculated considering van der Waals-Lifshitz attractive forces, electrostatic repulsive forces, and magnetic forces. (Assumptions: $\psi_0 = -0.522$ V; $A = 1.0 \times 10^{-20}$ J).
SUPPLEMENTAL FIGURES

Figure 3-S1. Experimental set-up for oxidation studies
Figure 3-S2 A) FT-IR spectra of NaOH-magnetite, TMAOH-magnetite, and the corresponding spectra for oxidized samples. B) FT-IR spectrum of TMA⁺.
Figure 3-S3. A) X-ray diffractograms for NaOH-magnetite, TMAOH-magnetite and a magnetite reference. B) Plot of Dcosθ vs. sinθ.
Figure 3-S4. Raman spectra of NaOH-magnetite and TMAOH-magnetite and corresponding change in spectra during oxidation.
Figure 3-S5. Magnetization curves at 5 K for NaOH-magnetite and TMAOH-magnetite.
Figure 3-S6. Magnetization curves at 5 K for magnetite (TMAOH) aerated at 84.4 °C for 4 hours. The inset illustrates the coercivity field $H_C$ and remanent magnetization $M_R$. 
Figure 3-S7. Potential energy profiles calculated considering van der Waals-Lifshitz attractive forces, electrostatic repulsive forces, magnetic forces, and repulsive hydrophobic forces. (Assumptions: $\psi_0 = -0.522$ V; $A = 1.0 \times 10^{-20}$ J).
Chapter 4 Aggregation and Sedimentation of Magnetite Clusters

Robert L. Rebodos and Peter J. Vikesland

Abstract

In recent years, synthetic magnetite nanoparticles have been used in a number of studies for the in-situ treatment of contaminated groundwater. A full understanding and characterization of particle reactivity however has been deterred by the tendency of the nanoparticles to aggregate as clusters of multiple nanoparticles. The effects of aggregation on nanoparticle reactivity have recently been documented in a number of studies. Unfortunately, the majority of these studies failed to address the dynamic nature of this aggregation process. For redox active nanoparticles like magnetite, aggregate properties can be simultaneously altered during a chemical transformation. In this study, we characterized the aggregation and sedimentation behavior of magnetite clusters using dynamic light scattering (DLS) and UV-VIS-NIR spectroscopy. The clusters were then oxidized and changes in morphology and other aggregate properties were monitored throughout the oxidation reaction. Results suggest that although the individual particle size remains constant after oxidation, indicative of a topotactic process, the cluster size and the aggregation and sedimentation kinetics were altered. Oxidized magnetite tends to be more resistant to aggregation. This result is consistent with the previous chapter quantifying the effects of oxidation on the magnetite particle interactions. These observations could have implications on understanding the overall reactivity, fate, and transport of magnetite nanoparticles in the subsurface environment.
1. Introduction

In recent years, synthetic magnetite nanoparticles have been used in a number of studies for the in-situ treatment of contaminated groundwater. Due to its high surface area, nanomagnetite has been shown to be an effective ex-situ sorbent of metalloid contaminants [1]. Although the application of magnetite nanoparticles for environmental remediation is promising, a full understanding and characterization of particle reactivity has been deterred by the propensity of the nanoparticles to aggregate as clusters of multiple nanoparticles that are unstable in suspension due to their large size (potentially > 1 μm). Cluster formation affects not only nanoparticle transport and delivery, but also potentially reactivity due to the loss of the specific activity of an individual particle [2-5].

The relative stability or instability of a magnetite suspension is dependent on the interplay of attractive and repulsive forces between particles. To evaluate the magnitude of the resulting interparticle interactions, previous studies have used extended Derjaguin, Landau, Verwey, Overbeek (DLVO) theory [6]. Classic DLVO theory only considers electrostatic repulsion between the electric double layers of two adjacent particles and attractive Lifshitz-van der Waals forces. This theory has subsequently been extended to incorporate so-called non-DLVO interactions such as short-range repulsive forces of hydration [7]. For superparamagnetic particles such as magnetite, it is also necessary to consider magnetic interactions [8]. Incorporating all four types of interparticle interactions, the overall potential energy of interaction, $V_T$, can be defined as

$$V_T = V_{vdW} + V_{ES} + V_{AB} + V_M$$  \hspace{1cm} (1)
where $V_{\text{vdw}}, V_{\text{ES}}, V_{\text{AB}}, \text{and } V_M$ are the Lifshitz-van der Waals, the electrostatic double layer, the hydration, and the magnetization energies, respectively. Positive $V_T$ values are generally indicative of stable suspensions, while negative $V_T$ values indicate colloidal instability [9-11].

An aggregation event can result either in the formation of irreversibly bound aggregates produced by close contact or in reversibly bound agglomerates that can be broken by sonication or other mixing processes [16]. Whether particles aggregate irreversibly or reversibly is dependent upon the shape of the overall interaction force profile obtained by solving equation 1 as a function of the separation distance between the aggregating surfaces. Given the challenges associated with experimentally differentiating aggregates from agglomerates and inconsistencies in the literature as to how these terms should be used [12] we refer to irreversibly bound masses of nanoparticles as clusters and the physical process bringing clusters together as aggregation.

Colloidal instability usually results in the formation of structures that are fractal in nature [13-15]. Fractal structures are defined in terms of a fractal dimension ($d_f$) which is the power to which its size ($R$) is raised such that it scales with mass ($m$)[16].

$$m \propto R^{d_f} \tag{2}$$

Often the fractal dimension of a cluster depends on the mechanism by which the aggregation process occurred - namely whether it is diffusion limited cluster aggregation (DLCA) or reaction limited cluster aggregation (RLCA)[16, 17]. DLCA or fast aggregation occurs when no repulsive force is experienced by the particles or clusters. The aggregation rate is solely dependent on the diffusion of the clusters to one another. At high electrolyte concentrations, coagulation in the DLCA regime leads to structures with low fractal dimension (i.e., loose and open aggregates; $d_f \approx 1.7-1.8$)[18]. For RLCA or slow aggregation, however, additional repulsive forces prevent the particles from coagulating. The formation of the aggregates is therefore dictated by the
probability of clusters adhering to one other. Structures formed by RLCA are more compact and have higher fractal dimensions ($d_f \approx 2.1-2.2$)[18]. Accordingly, $d_f$ can be used as a measure to evaluate how aggregates form[16].

Light scattering methods have been applied extensively to characterize aggregation processes in different systems [9, 10]. Dynamic light scattering (DLS) is a technique in which temporal fluctuations of scattered light are analyzed to obtain the diffusion coefficient and consequently the hydrodynamic diameter of a given sample. In some instances, DLS may also be used to determine fractal dimensions [19]. Being a non-invasive technique, DLS was employed in these studies to characterize the aggregation behavior of in-house synthesized magnetite [20, 21]. An inherent limitation of DLS, however, is that the method requires samples that have low particle concentrations in order to prevent multiple scattering events from occurring that lead to inaccurate measurements. Given this restriction, UV-VIS-NIR spectroscopy was also utilized to study the aggregation and sedimentation of magnetite at higher particle concentrations. This was achieved by monitoring the change in the incident light intensity as it passes through a given sample over time. In a suspension of relatively high particle concentration, the growth of the magnetite cluster ultimately leads to gravitational settling. This sedimentation process can be analyzed by plotting the absorbance readings as a function of time.

As discussed in Chapter 3, magnetite readily reacts with $O_2$ to produce maghemite. Because maghemite has a reported magnetic saturation that is less than that of magnetite we hypothesized that oxidation would decrease the magnitude of the magnetic attractive force between adjacent particles. As such, a difference in the aggregation and sedimentation behavior of magnetite after oxidation were expected. In addition, potential restructuring of the clusters
during and after oxidation may occur. Very few studies, if any, have delved into this restructuring phenomenon and this is particularly true for magnetite.

2. Materials and Methods

2.1. Reagents

Reagent grade chemicals were used without additional purification in all experiments. The following chemicals were used for the synthesis of magnetite: ferrous chloride tetrahydrate (FeCl$_2$·4H$_2$O; ICN Biomedicals), ferric chloride (FeCl$_3$ anhydrous; Fisher Scientific), sodium hydroxide (NaOH; Fisher Scientific; ≥ 98.5%), sodium chloride (NaCl; Fisher Scientific), and tetramethylammonium hydroxide pentahydrate (TMAOH·5H$_2$O; Fisher Scientific). All solutions used in the experiments were produced using de-aerated, deionized water (≥ 18.1 MΩ) made by boiling for 30 minutes and then sparging with either argon or nitrogen gas for at least 30 minutes while boiling continued. De-aerated water was removed from the heating source, capped, transferred to the anaerobic chamber (95% N$_2$/5% H$_2$; Coy Laboratory Products) and allowed to cool.

2.2 Magnetite synthesis

Magnetite nanoparticles were synthesized using a co-precipitation method adapted from Vayssieres, et al. [22]. In brief, a mixture of 0.1 M FeCl$_2$ and 0.2 M FeCl$_3$ was added drop-wise (~1 drop/s) to a well-mixed solution of 1 M NaOH and 1 M NaCl. The final ratio of iron solution to base solution was kept at 3:2 to maintain the pH above 12. Polypropylene containers were used to avoid silicate leaching from glass vessels because of the high pH synthesis conditions. Excess salts were removed by magnetically separating the precipitated nanoparticles and by rinsing with argon-purged, deionized water until the supernatant pH was in the 7-8.5 range.
TMAOH functionalized nanoparticles were synthesized using the same co-precipitation method except 1 M TMAOH was used instead of 1 M NaOH. Prepared magnetite stocks were stored in the anaerobic glovebox for periods up to 2 months. The mass concentration of a magnetite stock was gravimetrically determined in triplicate by drying 2 mL of slurry in a 75 °C oven. The final mass of dried sample was converted into an equivalent magnetite mass using the \( \text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3 \) gravimetric ratio and assuming 100% conversion of Fe\(_3\)O\(_4\) into \( \gamma\text{-Fe}_2\text{O}_3 \).

2.3 Characterization of magnetite powders

The morphology, size and electron diffraction patterns of nanoparticulate magnetite were characterized using a Philips 420T TEM operated at 100 keV. Particle slurries were mounted on carbon coated TEM grids (Electron Microscopy Science, Hartfield, PA) and dried in an aerobic environment for a minimum of 48 hours. Collected images were digitally transferred using a slow scan 3086 × 2056 pixel camera. The magnetite particle size was determined by analysis of collected TEM images using the ImageJ software package. High resolution transmission electron microscope (HRTEM) images were obtained using a FEI Titan scanning/transmission electron microscope (S/TEM) operated at 200 kV. Copper grids (400-mesh) with an ultrathin carbon film on a holey carbon support (Ted Pella, Inc.) were selected for samples investigated with the HRTEM. A representative selection of particle images was obtained from multiple sites on each grid.

Dried powder samples of nanoparticulate magnetite were characterized by XRD using a Rigaku RAPID Curved IP X-ray powder diffractometer with Cu K\(\alpha\) radiation and an image plate detector. Infrared and confocal Raman spectra of the dried magnetite samples were obtained using a Midac M2004 ATR FT-IR spectrometer with a diamond prism and a WITec alpha500R confocal Raman/AFM, respectively.
2.4 Determination of magnetite cluster-cluster aggregation kinetics

The aggregation behavior of the synthesized magnetite nanoparticle suspensions was studied using an ALV CGS-3 system. This system employs a 22 mW HeNe Laser, an APD-based single photon detector, and an ALV-5000/EPP correlator. The initial size and electrolyte-induced growth of the magnetite clusters were determined by cumulant analysis of dynamic light scattering (DLS) data collected at a 90° scattering angle every 15 seconds for a period of 30-60 minutes. All measurements were conducted at 25 °C. Each sample for analysis was placed in a new prewashed glass vial, rinsed with filtered (Whatman nylon membrane, 0.2 µm) deionized water prior to the addition of suspension. The effect of particle concentration on the aggregation rate was determined by diluting a given amount of sonicated stock suspension to obtain a final solid concentration of $10^{12}$-$10^{14}$ particles/mL. Stock solutions of NaCl, MgCl₂, CaCl₂, and FeCl₂ were prepared using reagent grade salts and deaerated, deionized water. The solutions were double filtered with 0.1 µm Whatman nylon membrane and Anodisc membrane filters. To determine the effect of each electrolyte on magnetite cluster aggregation, known volumes of salt solution, corresponding to the desired salt concentration, were added to the pre-sonicated suspensions. All vials were vortex mixed for approximately five seconds upon salt addition to ensure adequate mixing.

2.5 Determination of magnetite cluster sedimentation rates

Sedimentation of the magnetite clusters was monitored using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Magnetite suspensions with concentrations ranging from 5-500 mg/L were prepared inside the anaerobic glovebox by diluting a sonicated (one minute in a FS20H Fisher Scientific sonicator bath) magnetite stock solution. The dilute suspension was then sonicated for an additional 3 minutes prior to transferring a 3 mL aliquot to a quartz cuvette
sealed with a rubber septum. Outside the glovebox, a syringe was used to add a given volume of deaerated 0.1 M NaCl to the magnetite suspension to vary ionic strength and induce sedimentation. Prior to placement of the cuvette in the UV-Vis-NIR, it was wiped with a non-abrasive, lintless paper. Absorption spectra were periodically obtained between 200 and 1350 nm for periods up to 60 minutes. In some experiments, absorption measurements at 15 second intervals were obtained at wavelengths of 508, 1250, and 1320 nm for periods up to 60 minutes. Baseline corrections employing distilled deionized water were performed prior to sample analysis.

2.6 Magnetite oxidation experiments

Oxidation experiments employing TMAOH-magnetite (pH = 8.5) were performed by transferring 250 mL of deaerated, deionized water to a five neck round bottom flask inside the anaerobic glovebox. The flask was then sealed prior to removing it from the glovebox. Once removed from the glovebox, the flask was set upon a Barnstead Electrothermal heating mantle in a fume hood. The four necks of the flask were fitted with a glass diffuser rod, condenser, thermocouple and stainless steel sampling tube. Moist house air was bubbled through the air diffuser in the side stem of the flask. The condenser occupying the middle neck of the flask was connected to a circulating cold-water bath. To adjust the temperature of the suspension inside the flask, the thermocouple was attached to a Cole-Palmer Temperature Controller that regulated the heating mantle. To maintain the desired temperature, the flask was wrapped in aluminum foil. Once the desired temperature of 84°C in the flask was reached, a given amount of stock magnetite suspension, pre-sonicated for less than one minute, was added to the flask. Immediately after adding the stock, an initial sample of ≈ 40 mL was removed via the sampling
tube and transferred to the anaerobic glovebox. Periodic 40 mL samples were then taken over a four hour period.

3. Results

3.1 Magnetite primary particle characterization

As described in detail in Chapter 3, ImageJ analysis of TEM images indicated that NaOH-magnetite has a particle radius of 5.0 ± 0.75 nm, while TMAOH-magnetite is smaller with a particle radius of 3.97 ± 0.67 nm. XRD, FTIR, and Raman measurements confirmed that the particles consist of magnetite/maghemite, and Scherer analyses of the collected x-ray diffractograms were consistent with the relative sizes determined via TEM. FTIR measurements for TMAOH-magnetite indicate that a layer of adsorbed TMA⁺ cations exists at the surface of this material.

High resolution TEM (HRTEM) was used to further characterize TMAOH-magnetite. As indicated by the appearance of lattice fringes in the particles shown in Figure 4-1a, TMAOH-magnetite is crystalline with the crystalline order extending to the edge of the nanoparticle.

3.2 Magnetite cluster characterization

In aqueous suspension, magnetite exists as clusters of multiple primary particles with DLS determined hydrodynamic radii (intensity based) of 100-200 nm for NaOH-magnetite and 30 nm for TMAOH-magnetite (results not shown). The smaller cluster size of TMAOH-magnetite is attributed to the presence of the TMA⁺ cation at the nanoparticle surface. This surface associated cation sterically restricts particle-particle interactions and facilitates nanoparticle dispersion [23]. The stability of the adhered TMA⁺ layer was found to be a function of the number of wash cycles employed to clean the nanoparticles following synthesis. As shown in Figure 4-2, each wash step
sequentially resulted in an increase in the measured hydrodynamic radius for the TMAOH-magnetite particles. Immediately following synthesis, the measured hydrodynamic radius was 18 nm (≈4.5× larger than the individual particle radius), but depletion of the TMAOH concentration following additional wash cycles increased the measured radius to 30 nm (≈7.5× larger than the individual particle radius). As determined via ImageJ analysis of collected TEM images, these sequential washes do not statistically alter the intrinsic particle diameter (results not shown). In the experiments described hereafter, at least four wash steps were employed.

The surface charge of the nanomagnetite suspensions was determined as a function of the solution ionic strength and pH. As shown by plotting the measured zeta potential versus the solution pH (Figure 4-3), the pH_{IEP} – or the pH where the net charge on the nanoparticles was zero – was 6.8 ± 0.3 for NaOH-magnetite and 6.6 ± 1.0 for TMAOH-magnetite. Each of these values is within the range of pH_{IEP} values previously reported for magnetite [24]. Below the pH_{IEP} the surface is positively charged, while above the pH_{IEP} the surface is predominantly negatively charged. The lower pH_{IEP} for TMAOH-magnetite is consistent with the presence of an adsorbed layer of TMA\(^+\) cations at the iron oxide surface. The complexation of organic materials at an oxide surface generally results in a lowering of the measured pH_{IEP} [24].

Magnetite has a nondescript UV-VIS-NIR spectrum consisting of absorbance bands in three spectral regions that are indicative of electronic transitions within the crystalline lattice. These bands are the Fe\(^{III}\) crystal or ligand field transitions, the interaction of magnetically coupled Fe\(^{III}\) atoms, and ligand-metal charge transfer excitations from the O(2p) non-bonding valence bands to the Fe(3d) ligand field orbitals or possibly between Fe\(^{II}\) and Fe\(^{III}\) [25]. Figure 4-4 illustrates exemplary UV-VIS-NIR spectra for NaOH-magnetite and TMAOH-magnetite. Qualitatively the spectra are similar except for the enhanced absorbance below 300 nm for TMAOH-magnetite
due to the TMA$^+$ cations associated with the particle surface (Figure 4-5b). There are two absorption maxima in the magnetite spectrum over this wavelength range – one centered at 380 nm corresponding to Fe$^{III}$ ligand field transitions and another at $\lambda > 1320$ nm that corresponds to an intervalence charge transfer band [26].

Extinction (= absorption + scattering) spectra for NaOH-magnetite and TMAOH-magnetite were determined by varying the magnetite concentration from 5-250 mg/L. As shown in Figure 4-5a, TMAOH-magnetite has a higher absorptivity in the UV region than NaOH-magnetite, while in the near-IR it is lower. The former effect is attributed to the absorbance of the TMA$^+$ cations (Figure 4-5b), while the latter could be the result of the decreased particle size for TMAOH-magnetite or to its smaller cluster size. Each of these possibilities would result in less light absorption for a given mass of particles.

During storage the magnetite stock suspensions, particularly NaOH-magnetite, aggregate significantly. To breakup these agglomerates and attain a stable initial cluster size the experimental solutions were sonicated prior to each experiment. As shown in Figure 4-6a, the initial absorbance at 508 nm of a NaOH-magnetite solution varies with both the sonication time and the particle concentration. This observation is consistent with Mie theory, which suggests that individual nanoparticles will primarily absorb light, while clusters of those same particles will also scatter light thereby leading to decreased absorption relative to the dispersed nanoparticles [16]. As will be discussed later, the observation that the absorption of a magnetite suspension is affected by its aggregation state is important since it suggests that the changes in absorption that occur as a result of aggregation and sedimentation maybe non-linear in nature. As shown in Figure 4-6b, the stability of a given suspension is a function of the sonication time.
Collectively considering Figures 4-6a and 4-6b, a sonication period of three minutes was chosen for all experiments described herein.

3.3 Magnetite cluster-cluster aggregation

We determined the aggregation behavior of our magnetite clusters as dictated by solution pH and the presence of electrolytes. The aggregation of these clusters led to an increase in the hydrodynamic radius that was measured using dynamic light scattering.

3.3.1 pH effects

To illustrate the effect of pH on cluster-cluster aggregation, we sequentially added aliquots of 0.1 M NaOH to a $10^{15}$ particle/mL NaOH-magnetite suspension (11 mM) and measured the hydrodynamic radius of the suspension over time (Figure 4-7). Prior to the addition of NaOH, the hydrodynamic radius was $130 \pm 7$ nm at a pH of 5.9. Increasing the pH to 6.15 results in a slight increase in the hydrodynamic radius. The rate at which this increase occurs, however, was only 0.01 nm/s. Further addition of NaOH to pH 6.27 and beyond accelerated the rate at which the clusters aggregate and increased the measured hydrodynamic radius. At both pH 6.27 and pH 6.36 the change in the hydrodynamic radius was initially quite rapid ($k_{\text{pH}=6.27} = 2.72 \text{ nm/s}$, $k_{\text{pH}=6.36} = 7.058 \text{ nm/s}$). At pH 6.44, the first four readings exhibited a slope of $k_{\text{pH}=6.44} = 13.28 \text{ nm/s}$, but became unstable thereafter as the overall cluster size approached the maximum limit of the DLS instrument employed. The aggregation behavior shown in Figure 4-7 is consistent with past studies examining the aggregation of nanoparticles and nanoparticle clusters [9, 10] [27]. The rate of change in the hydrodynamic radius of the aggregate increased as the pH approached the isoelectric point of NaOH-magnetite, which is pH 6.8 (Figure 4-3). This behavior is consistent with DLVO theory which suggests that at the isoelectric point the clusters will aggregate most rapidly due to the decreased thickness of the repulsive double layer [28].
3.3.2 *Indifferent electrolyte effects*

We also investigated the salt induced aggregation of our NaOH- and TMAOH-magnetite clusters. Figure 8 depicts illustrative results for the aggregation of NaOH-magnetite following NaCl addition. As shown, at low salt concentrations the kinetics of aggregation are quite slow. As expected, however, at higher salt concentrations the aggregation kinetics become faster.

To quantify magnetite cluster-cluster aggregation we monitored the aggregation kinetics for $t > 15$ seconds to determine the aggregation rate constant [10, 28]:

$$\left(\frac{dN_1}{dt}\right)_{t \to 0} = -k_{11}N_0^2$$

(3)

where $k_{11}$ is the measured aggregation rate constant obtained by fitting a linear regression to DLS acquired hydrodynamic radius data. $N_0$ is the concentration of nanomagnetite clusters at time $t=0$ and $N_1$ is a dimer formed by aggregation of two clusters. Under high salt conditions where aggregation is limited only by the diffusion of two clusters (diffusion limited cluster aggregation, DLCA) the value of $k_{11}$ is maximized and is referred to as $k_{11,\text{fast}}$. For conditions where repulsive interaction forces control aggregation (reaction limited cluster aggregation, RLCA) $k_{11}$ is slower. One can define the stability of a suspension using the stability ratio $W$:

$$W = \frac{k_{11,\text{fast}}}{k_{11}}$$

(4)

After applying equation 4 to our collected DLS data we plotted the stability ratio versus salt concentration for three different salts (NaCl, MgCl$_2$, and CaCl$_2$) in Figure 4-9.

3.3.3 *Effect of particle concentration*

NaCl addition was used to aggregate solutions with NaOH-magnetite particle concentrations ranging from $10^{12}$-10$^{14}$ particles/mL. These experiments were conducted to determine how concentration affects the aggregation behavior of the magnetite clusters (Figure 4-10). As shown
in Figure 4-10, the aggregation rate constants generally increase with an increase in magnetite concentration, but the increase is less than the predicted 100× from equation 3. This result is presumably due to the fact that equation 3 was initially developed to describe a particle-particle aggregation process that differs from the cluster-cluster aggregation studied here.

3.3.4 NaOH-magnetite vs. TMAOH-magnetite

Experiments were conducted to compare the aggregation behavior of NaOH-magnetite versus that of TMAOH-magnetite. As shown in Figure 4-11A, the aggregation of TMAOH-magnetite in general occurs at a rate that is much slower than that of NaOH-magnetite. Such a result is consistent with the presence of a stabilizing TMA⁺ cation layer at the surface of TMAOH-magnetite. This layer sterically restricts the aggregation of the TMAOH-magnetite clusters. Interestingly at low salt concentrations, however, the kinetics of aggregation are enhanced for TMAOH-magnetite. This differential effect is illustrated in Figure 4-11B, which plots the data in terms of stability ratio.

3.3.5 Fe⁺II addition

In contrast to the aggregation behavior observed following addition of the indifferent electrolytes CaCl₂, MgCl₂, and NaCl, the addition of FeCl₂ resulted in a highly differential trend. It was observed that the suspension generally became more stable as implied by the decrease in cluster size as the Fe⁺II concentration was increased (Figure 12). The addition of Fe(II) apparently resulted in a change in the surface properties of the magnetite nanoparticles as suggested elsewhere [29]. A change in the oxidation state of magnetite, for example, may have produced clusters with higher colloidal stability than pristine nanomagnetite. This observation will be further analyzed in the Discussion section.
3.4 Magnetite cluster sedimentation

An inherent problem with DLS is that the method requires samples that have low particle concentrations in order to prevent multiple scattering events from occurring that lead to inaccurate measurements. Given this limitation, we examined the aggregation and sedimentation behavior of magnetite at higher particle concentrations by monitoring the change in optical absorbance as a function of time using UV-VIS-NIR spectroscopy. A representative spectrum is shown in Figure 4-13.

The coagulation and sedimentation of both NaOH-magnetite and TMAOH-magnetite clusters was initiated by sodium chloride addition. The addition of salt at concentrations ranging from 2 to 20 mM causes a decrease in absorption at 508 nm for both NaOH-magnetite (Figure 4-14) and TMAOH-magnetite (results not shown). The detrimental effect of salt addition on the colloidal stability of magnetite was expected since an increase in the ionic strength of the solution lowers the repulsive electrostatic barrier and enables rapid coagulation. Relative to the salt-free solution, the observed sedimentation kinetics were enhanced upon addition of ≥2 mM salt; however, there was no discernable trend observed in the sedimentation curves for salt concentrations between 2 and 20 mM (Refer to Figures 4-15 to 4-17).

3.5 Magnetite oxidation

3.5.1 Effect of oxidation on particle size and surface properties

Magnetite is a redox active species and is readily oxidized by oxygen to produce maghemite, we accordingly studied the effects of oxidation on magnetite aggregation and sedimentation. Visually the oxidation of magnetite results in a change in the color of the suspension from black to brown to orange brown. This topotactic oxidation process is of particular interest because although the transformation yields particles of the same nominal size, their surface properties
may be different. Figure 4-18 shows the change in the measured zeta potential and Fe(II) concentration of a TMAOH-magnetite suspension during oxidation at a constant temperature of 90 °C. At a fixed pH of 8.43 ± 0.25, the zeta potential for oxidized magnetite is 42% lower in magnitude than that for unoxidized magnetite. This corresponds to a change in the zeta potential value from -42 mV to -27 mV. This decrease in the magnitude of the zeta potential can be attributed to the change in surface charge resulting from conversion of Fe(II) to Fe(III). To further examine the effects of oxidation on the magnetite surface properties, pH versus zeta potential curves were determined for a NaOH-magnetite suspension heated at 90 °C for a period of 5 hours. The isoelectric point was determined to shift to a higher pH during oxidation (Figure 4-19).

**3.5.2 Effect of oxidation on aggregation**

Because the surface and magnetic (Chapter 3) properties of magnetite are altered by oxidation, we expected to see differences in the aggregation behavior of our magnetite suspensions before and after oxidation. We characterized this effect by monitoring the changes in cluster size and stability during the oxidation process. The initial cluster size was observed to increase following oxidation (Figure 4-20A). The salt induced aggregation rate, however, decreased with oxidation time thus suggesting that unoxidized clusters aggregate more rapidly than oxidized ones. Furthermore, the stability of the suspension can be inferred from the extent of salt effects in the aggregation behavior of the clusters as shown by the error bars in Figure 20B. Note that not only do the oxidized particles have lower aggregation rates, the effects of salt addition are also considerably less the more oxidized particles.

**3.5.3 Effect of oxidation on sedimentation**
Changes in the aggregation state of magnetite are expected to affect the sedimentation behavior as well. Using higher magnetite concentrations than were experimentally accessible in the aggregation studies, we looked at the effects of oxidation on the coagulation and sedimentation behavior of magnetite based on the change in the UV-VIS-NIR spectra and absorbance readings at 508 nm. The results are shown in Figure 4-22 where a 300 mg/L TMAOH-magnetite suspension was oxidized for 4 hours. The trends in terms of aggregation and sedimentation rates are further described in the discussion below.

4. Discussion

4.1 Magnetite clusters

In both the NaOH-magnetite and TMAOH-magnetite suspensions, magnetite is present in the form of clusters of nanoparticles with hydrodynamic radii varying from 100-200 to 30-35 nm, respectively. These clusters were resistant to disaggregation via bath sonication or solution agitation and may have formed during the synthesis of the materials. Although the nucleation events leading to particle formation were rapid enough to ensure a small particle size [22] the high-salt concentration synthesis conditions were such that electrical double layer repulsion was minimized and the particles immediately aggregated. Many existing references describing nanoparticle clusters report sizes that are considerably larger than the nascent nanoparticle size. [20]

4.2 Aggregation of magnetite clusters.

As shown in Figure 4-8, salt addition induced aggregation of our magnetite clusters. As expected, the magnitude of this effect was a function of the salt concentration and valence with enhanced aggregation rates at higher ionic strengths and higher valence (Figure 4-9). One
striking feature of the results presented in Figure 4-8 is the observed immediate increase in the measured cluster size at t = 15 seconds that occurs following the addition of salt concentrations in excess of 6 mM. This increase occurs regardless of the sample conditions and is a unique feature of these magnetite suspensions. We attribute this feature to the rapid relaxation of an individual magnetite cluster in response to salt addition and not to a slower cluster-cluster aggregation process. Addition of salt into the pore space of the cluster altered the osmotic conditions leading to rapid swelling. Such an effect has previously been observed for titanium oxide clusters [30]. Consequently, this phenomenon made it difficult to determine the fractal dimensions of the magnetite clusters using our DLS data. In systems where the cluster’s radius of gyration approximates the average hydrodynamic radius measured by DLS, a logarithmic plot of the hydrodynamic radius against time can be used to estimate the fractal dimension. [19]

Applying equation 4 to our collected data for NaOH-magnetite we plotted the stability ratio versus salt concentration for three different salts (NaCl, MgCl₂, and CaCl₂) in Figure 4-9. As shown, the calculated stability ratios decrease with increasing salt concentration up to a limiting value of 1. At salt concentrations beyond this point, aggregation is limited only by diffusion since the repulsive electrostatic energy barrier has been removed and further addition of salt no longer affects the aggregation rate. The salt concentration where this elimination occurs is defined as the critical coagulation concentration (CCC) and is experimentally determined by extrapolating the measured stability ratios at low salt concentrations to a value of 1. Using this approach, we determined the CCC values for the salts to be: NaCl = 9.35 mM, MgCl₂ = 0.631 mM, and CaCl₂ = 0.313 mM. This trend is consistent with past reports and with the empirical Shulze-Hardy rule that predicts the CCC should scale with the sixth power of the valence [16].
The effect of Fe(II) on the stability of the suspension differs from that of the inert co-solutes previously discussed. In contrast to the cluster growth observed with inert electrolytes the addition of Fe(II) actually reduced the hydrodynamic radius of the clusters. The diffraction pattern obtained from the TEM image of magnetite suspended in Fe(II) containing aqueous solution differ from those in CaCl₂ solutions (Figure 4-12 Inset). This difference implies a loss of crystallinity and the formation of an amorphous coating as a result of Fe(II) sorption. As discussed in Chapter 3, sorption of Fe(II) decreases the saturation magnetization and the magnetic attractive force between particles. This decreased force results in a smaller cluster size that does not aggregate as readily as the larger clusters.

4.3 Sedimentation of magnetite clusters

The collected sedimentation curves can be subdivided into three regions that are demarcated by changes in slope [11]. The first region (aggregation I) corresponds to the initial coagulation of the magnetite aggregates. In this region the aggregates are coagulating, but have not reached the critical size needed to initiate rapid sedimentation. Once the critical size is reached, at time $t_{\text{crit1}}$, sedimentation occurs rapidly (sedimentation I). For some suspensions, particularly those with high salt and mass concentrations, a third region with a slower sedimentation rate can be observed (sedimentation II). This region, initiated at time $t_{\text{crit2}}$, has previously been interpreted as the sedimentation of particles that failed to attain critical size.

As noted previously, changes in salt concentration only had a moderate effect on the sedimentation of NaOH-magnetite (Figure 4-15). This effect is surprising since we previously had shown using dynamic light scattering (Figure 4-9) that the CCC for NaOH-magnetite was 10 mM and thus we had anticipated that there would be differences in the sedimentation curves obtained below the CCC (reaction-limited cluster aggregation (RLCA) conditions) relative to
those obtained above the CCC (diffusion-limited cluster aggregation (DLCA) conditions). Since
the magnetite concentration used in the sedimentation studies are higher compared to the DLS
studies, the salt effects may have been masked by this relatively high mass loading. As seen in
Figure 4-15, changes in particle concentration had a larger and more systematic effect on the
measured sedimentation rates. Sedimentation experiments were performed to measure the
aggregation rates of magnetite suspensions with particle concentrations ranging from 50-500
mg/L and NaCl concentrations ranging from 0-30 mM. The aggregation rates were obtained by
determining the slope of the change in absorbance measured at 508 nm, over time up to $t_{\text{crit1}}$. A
direct relationship between particle concentration and aggregation rate is shown in Figure 4-16.
As shown, the effect of particle concentration was significant for each tested salt concentration
and, as observed previously, there was little difference in the aggregation kinetics measured for
10-30 mM NaCl.

Figure 4-17 shows the change in $t_{\text{crit1}}$ with increasing particle concentration. Higher particle
centration suspensions require shorter time to reach the critical size needed for settling. Both
sedimentation rate and critical time values plateau at high magnetite concentrations suggesting
that above a certain mass concentration, sedimentation always occurs at the same timepoint.

Magnetite nanoparticles synthesized using TMAOH were more stable relative to those
produced with NaOH. In general, the TMAOH-magnetite particles increased in size at a slower
rate relative to NaOH-magnetite meaning that the critical size needed for settling is reached more
slowly (Figure 4-11).

4.4 Magnetite oxidation.

Oxidation resulted in changes in the aggregation and sedimentation behavior of magnetite.
Figure 4-21 shows that for TMAOH-magnetite, the cluster size measured by DLS increases
during oxidation. This change in hydrodynamic radius can be attributed to the transformation in the morphology of the aggregate such that the resulting cluster may have a lower fractal dimension (i.e., more branched and less dense structure). This could be a consequence of a decrease in the attraction between the clusters or a lowering of the cluster-cluster interaction energy. This trend was further assessed by measuring the cluster size before and after sonication. For clusters aggregated reversibly, sonication is sufficient to break agglomerates into smaller units. As shown in Figure 4-21, oxidized magnetite flocs were more prone to disaggregation. Furthermore, the measured sizes of the oxidized species were smaller compared to the original clusters.

The effect of oxidation was further analyzed using sedimentation curves acquired by UV-Vis-NIR spectrophotometry. Figure 4-23 suggests that the aggregation rate is generally lower for oxidized particles relative to as-synthesized particles. For TMAOH-magnetite, the aggregation rate drastically decreased once oxidation began and the critical time (t_{crit}) also increased in magnitude as oxidation continued (Figure 4-23). The trends in the sedimentation rates (Figure 4-24 and 4-25), however, are more complicated and perhaps could be a result of a number of factors such as changes in the specific cluster morphology (i.e., fractal dimension) and behavior brought about by the oxidation process. The potential for cluster restructuring during the oxidation process is possible and preliminary Small Angle X-Ray Scattering (SAXS) experiments by our laboratory suggest that a change in the fractal dimension of the clusters does occur during oxidation.

Further evaluation of the effects of concentration on the aggregation and sedimentation rates suggests that better linear correlations between mass concentration and aggregation rate are
achieved for the oxidized species. The expected 2\textsuperscript{nd} order dependency based on the simplified analytical solution described by Morel and Schiff [31]:

$$\frac{\partial C}{\partial t} = -BC^2$$  \hspace{1cm} (5)

where $B$ is the rate coefficient, $C$ is the mass concentration and $t$ is time, does not apply for these clusters. The deviation from the projected trend (Figure 4-26) observed more clearly for the unoxidized particles, may be a result of the higher cluster-cluster interaction for magnetite relative to that of maghemite. As described in the previous chapter, interactions such as magnetic dipole interactions, are diminished during oxidation causing the particles to behave more independently.

A comparison of the effects of oxidation on both TMAOH-magnetite and NaOH-magnetite is shown in Figure 4-27. Note that the aggregation rates for 200 mg/L TMAOH-magnetite are slower relative to that for NaOH-magnetite. The oxidized forms of both types of particles have lower aggregation rates relative to the unoxidized ones suggesting that changes in surface properties of magnetite during oxidation generally result in the formation of more stable clusters. This result is consistent with the DLS findings. In terms of the sedimentation behavior, however, the trends for TMAOH-magnetite differ from those of NaOH-magnetite. The disparity between these species may be attributed to the morphology of the cluster that is formed during the initial aggregation stages and also the specific cluster growth mechanism. Faster aggregation processes are expected to produce clusters with lower fractal dimension. The sedimentation of these clusters is expected to be different from the more densely packed (higher fractal dimension) structures formed during the slower aggregation process. After oxidation, the oxidized TMAOH-magnetite had a lower sedimentation rate while for NaOH-magnetite the
sedimentation rate was higher compared to their corresponding unoxidized species. These differences are due to the alteration in the surface properties of the particles during oxidation.

4.5 Implications on reactivity and the effects of aggregate restructuring

Very few studies on aggregate restructuring, particularly on magnetite, can be found in the literature. However, based on the trends observed in this work and the dynamic nature of magnetite clusters subjected to conditions that promote transformation, it is plausible that a given cluster undergoes morphological changes over time. Restructuring of aggregates has been documented elsewhere [32, 33]. In a given system, one can monitor the changes in fractal dimension of a given suspension over time. Although such techniques were beyond the scope of this work, specific aggregation and sedimentation trends observed particularly as a result of magnetite oxidation imply that the morphology of the original clusters was altered during this process. A possible rearrangement mechanism during aggregation is illustrated in Figures 4-28a and 4-28b. In Figure 4-28a, a hypothetical cluster growth is shown in which the oxidized magnetite retains its cluster structure or rearranges causing a change in morphology. In Figure 4-28b, oxidized sites (i.e., maghemite), having weaker attractive forces act as sites for cleavage and detachment resulting in the formation of new structures. This phenomenon could have a direct implication on the transport of the clusters for example in a porous media or via simple gravitational settling. Bigger cluster may have limited ability to pass through soil pores and even potential foul fluid pathways. In terms of reactivity, cluster restructuring could result in the breakup of the initial aggregate exposing previously unreacted sites. For a reaction that is mass transfer limited, agitation of highly compact aggregates could result in enhancement of reactivity and faster reaction rates. Overall, these observations and hypotheses should be further studied in
order to characterize the implications of these transformations on the overall reactivity, fate, and transport of magnetite nanoparticles in subsurface environments.

Additionally, since this study suggests that oxidation can affect magnetite aggregate structure and morphology, one may be able to manipulate or engineer the cluster form, strength and stability of magnetite by allowing the nanoparticles to undergo controlled oxidation in order to attain the desired cluster properties. For example, a compromise between the nanoparticle stability and reactivity can be achieved by controlling the oxidation state and consequently the aggregation state of the iron oxide, in order to treat a contaminant that is not easily accessible by large nanomagnetite clusters. To our knowledge, this novel concept has not been explored in other previous research studies.

5. Conclusion

In the absence of stabilizers, magnetite clusters aggregate and settle out of the solution. The rate of aggregation and sedimentation is dependent on the particle concentration and aqueous conditions such as pH and ionic strength. The oxidation state of magnetite also affects the colloidal stability of the suspension. Oxidized magnetite (i.e., maghemite) was observed to have a lower aggregation rate than unoxidized magnetite. The morphology of the oxidized clusters were also different from the initial state as shown by the variability in sedimentation behavior. These factors are important for understanding not only the transport mechanism of magnetite in natural systems, but also in predicting their potential reactivity to contaminants.
References

Figure 4-1. HRTEM images of TMAOH-magnetite A) prior to and B) following oxidation. Magnetite was oxidized by heating suspension with constant aeration at 90 °C for 4 hours.
Figure 4-2. Effect of washing on the cluster size of TMAOH-magnetite measured using DLS and the average diameter of TMAOH-magnetite determined via ImageJ analysis of collected TEM images (n = 20, 40, 60 for 1st, 2nd and 3rd washing, respectively).
Figure 4-3. Isoelectric point (IEP) of NaOH-magnetite (pH 6.8 ± 0.3). The IEP for TMAOH-magnetite was obtained to be pH 6.61 (need to include).
Figure 4-4. UV-VIS-NIR spectra of a) NaOH-magnetite and b) TMAOH-magnetite as a function of the magnetite concentration. Samples were sonicated for 120 seconds.
Figure 4-5. A) Extinction spectra for TMAOH-magnetite and NaOH-magnetite determined by varying the particle concentration between 5-250 mg/L. B) Absorption of TMA$^+$ as a function of concentration. The molar absorptivities for NaOH-magnetite are higher than those for TMAOH-magnetite in the visible and near-IR region, but is lower in the UV region. The increased absorptivity in the UV region is due to the presence of TMA$^+$. Prior to spectral acquisition the samples were sonicated for 120 seconds.
Figure 4-6. A) Effect of sonication time on the absorbance of NaOH-magnetite suspensions (10-300 mg/L) at 508 nm. B) Effect of sonication duration on the measured absorbance of a 150 mg/L NaOH-magnetite suspension over time.
Figure 4-7. The measured hydrodynamic radius of a NaOH-magnetite suspension increases over time following pH adjustment.

Figure 4-7 Inset: Rate of cluster growth (nm/s) increases over time following pH adjustment.
Figure 4-8  Measured hydrodynamic radius of a NaOH-magnetite suspension following salt addition (10^{15} particles, pH 8.0).
Figure 4-9. Measured stability ratios (W) of NaOH-magnetite in the presence of three different electrolytes. (10^{15} particles, pH = 8.0)
Figure 4-10. Increasing particle concentration results to an increase in the rate of aggregation for NaOH-magnetite in NaCl. The variations are less than the 100× increased predicted from equation 2. (pH = 7.5 ± 0.25)
Figure 4-11. A) NaOH-magnetite generally aggregates more quickly than TMAOH-magnetite. B) The measured CCC for TMAOH-magnetite is at a lower salt concentration than for NaOH-magnetite as shown in this stability ratio plot.
Figure 4-12. Measured aggregate size as a function of time for different initial concentrations of Fe$^{II}$. 


Figure 12 Inset. TEM images of newly synthesized magnetite nanoparticles and particles suspended in 10 mM CaCl$_2$ and 100 mM FeCl$_2$. The corresponding diffraction patterns are shown on the right.
Figure 4-13. The absorption spectra of a 200 mg/L (0.86 mM) TMAOH-magnetite suspension decrease in magnitude following addition of 20 mM NaCl.
Figure 4-14. Absorbance readings at $\lambda = 508$ nm of different NaOH-magnetite suspensions (200 mg/L = 0.86 mM) suspended in different concentrations of NaCl.
Figure 4-15. Sedimentation curves obtained at $\lambda = 508$ nm for magnetite concentrations ranging from 50-500 mg/L NaOH-magnetite in 10 mM NaCl.
Figure 4-16. Measured aggregation rates obtained from the initial slope of sedimentation curves of NaOH-magnetite with different mass concentrations (mg/L) where aggregation was induced by the addition of salt (0-30 mM NaCl).
Figure 4-17. First critical time, $t_{\text{crit1}}$, (aggregation-sedimentation) as a function of NaOH-magnetite mass concentration in 10-30 mM NaCl solutions.
Figure 4-18. Decrease in the magnitude of zeta potential of TMAOH-magnetite accompanied by the loss of Fe$^{II}$ during oxidation (90 °C, pH 8.43 ± 0.25).
Figure 4-19. Shifting of IEP of NaOH-magnetite to a higher pH during oxidation (100 °C for 5 hours).
A. Salt effects on the aggregation of magnetite heated from 0-240 minutes at 90 °C. Initial particles tend to aggregate faster compared to those that are heated and bubbled with air. 

B. Oxidized particles have slower aggregation rate than oxidized particles and are less affected by the addition of salt.

Figure 4-20. A) Salt effects on the aggregation of magnetite heated from 0-240 minutes at 90 °C. Initial particles tend to aggregate faster compared to those that are heated and bubbled with air. B) Oxidized particles have slower aggregation rate than oxidized particles and are less affected by the addition of salt.
Figure 4-21. Change in the hydrodynamic radius of the TMAOH-magnetite clusters during oxidation. Sonicating the particles resulted in disaggregation and cluster fragmentation. [0.2mM, 46 mg/L, heated at 60°C]
Figure 4-22. Aggregation and sedimentation curves for TMAOH-magnetite (300 mg/L, 10 mM NaCl)
Figure 4-23. Aggregation rate and Critical time, $t_{crit1}$ of different TMAOH-magnetite suspensions as a function of heating time.
Figure 4-24. Sedimentation rates obtained from the sharp slope (2nd region) of the sedimentation curves of TMAOH-magnetite as a function of heating time.
Figure 4-25. Second critical time, $t_{\text{crit}_2}$ of different magnetite suspensions as a function of heating time.
Figure 4-26. Scaling of the sedimentation rate of TMAOH-magnetite with respect to particle concentration.
Figure 4-27. Aggregation rate and sedimentation rate of unoxidized and oxidized TMAOH-magnetite and NaOH-magnetite (200 mg/L at 10 mM NaCl).
A. Hypothetical cluster growth in magnetite aggregation process where oxidized magnetite retains its cluster structure or rearranges causing a change in morphology.

B. Rearrangement in a magnetite aggregate with sites undergoing various oxidation stages. Although unlikely, preferential or selective rearranging may occur.

Figure 4-28