RICE UNIVERSITY

Metal ferrite nanoparticles as tracers in hydraulically fractured wells

by

Lauren Morrow

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

APPROVED, THESIS COMMITTEE

Andrew R. Barron, Chair
Charles W. Duncan Jr. – Welch Chair of Chemistry and Professor of Materials Science and NanoEngineering

Lon J. Wilson
Professor of Chemistry

Matteo Pasquali
Department Chair of Chemistry, Professor of Chemistry and Biomolecular Engineering and Chemistry

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ABSTRACT

Metal ferrite nanoparticles as tracers in hydraulically fracturing wells

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Lauren Morrow

A variety of metal ferrite nanoparticles were synthesized via thermal decomposition reaction and characterized with transmission electron microscopy, small angle X-ray scattering, inductively coupled plasma – optical emission spectroscopy, X-ray photoelectron spectroscopy, thermogravimetric analysis, and a superconducting quantum interference device in order to develop a cost-effective means of tracing hydraulic fractures in wells. In addition, the nanoparticles were developed as a means of determining sources of contamination in the environment surrounding a well by way of “fingerprinting” the different potential sources. This is achieved through the manipulation of the quantities of metal cations substituted into the crystal structure of magnetite, allowing for the creation of unique and desired magnetic characteristics. In order to determine the feasibility of using nanoparticles as tracers, the quantity needed to be able to detect the nanoparticles as determined, as well as how the magnetic properties change as temperature increases as a function of nanoparticle composition. Finally, the feasibility of making industrial quantities of the nanoparticles was investigated.
“The chemists are a strange class of mortals, impelled by an almost insane impulse to seek their pleasures amid smoke and vapor, soot and flame, poisons and poverty; yet among all these evils I seem to live so sweetly that may I die if I were to change places with the Persian king.”

— Johann Joachim Becher
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These past several years have been full of ups and downs, as well as inspiring discoveries and life changing events. If it wasn’t for the incredible support I received, this thesis would not have been possible. To that end, I would like to thank those who were instrumental in helping me get to this point.

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Å  angstrom(s), $10^{-10}$ m
acac  acetylacetonate
°C  degrees centigrade
$^{13}$C  carbon-13, stable isotope of carbon
C  Curie constant
c.a.  *circa*, approximately
$\chi$  magnetic susceptibility
$\chi_{mass}$  mass susceptibility
CFSE  crystal field splitting energy
$\text{cm}^3$  centimeters cubed
°  degrees
$\Delta\chi_{mass}$  change in mass susceptibility
$\Delta M_{mass}$  change in mass magnetization
EDX  energy-dispersive X-ray spectroscopy
e.g.  *exempli gratia*, for example
emu  electromagnetic unit
Eq.  Equation
et al.  *et alia*, and others
eV  electron volts
frac fluid  hydraulic fracturing fluid
frac sand  hydraulic fracturing sand
fracing  hydraulic fracturing
fracking  hydraulic fracturing
g  gram
$H$  magnetic field strength
<table>
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<th>Symbol</th>
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<tr>
<td>HDD</td>
<td>1,2-hexadecanediol</td>
</tr>
<tr>
<td>HPLC</td>
<td>high-performance liquid chromatography</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma – optical emission spectroscopy</td>
</tr>
<tr>
<td>i.e.</td>
<td><em>id est</em>, that is (to say)</td>
</tr>
<tr>
<td>$k$</td>
<td>reaction rate constant</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>kDa</td>
<td>kilodaltons</td>
</tr>
<tr>
<td>kg</td>
<td>kilogram(s), $10^3$ g</td>
</tr>
<tr>
<td>L</td>
<td>liter(s)</td>
</tr>
<tr>
<td>lb(s)</td>
<td>pound(s)</td>
</tr>
<tr>
<td>$M$</td>
<td>magnetization of material</td>
</tr>
<tr>
<td>M</td>
<td>metal</td>
</tr>
<tr>
<td>$M'$</td>
<td>metal, unique from M</td>
</tr>
<tr>
<td>m</td>
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</tr>
<tr>
<td>$m^3$</td>
<td>meters cubed</td>
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<td>$\mu$L</td>
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<td>$M_{mass}$</td>
<td>mass magnetization</td>
</tr>
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<td>mol</td>
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<tr>
<td>MRI</td>
<td>magnetic resonance imaging</td>
</tr>
<tr>
<td>$M_s$</td>
<td>magnetic saturation</td>
</tr>
<tr>
<td>mT</td>
<td>millitesla(s), $10^{-3}$ T</td>
</tr>
<tr>
<td>$\mu$</td>
<td>mu, effective magnetic moment</td>
</tr>
<tr>
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</tr>
<tr>
<td>$\mu_o$</td>
<td>mu naught, magnetic constant</td>
</tr>
<tr>
<td>$n$</td>
<td>number of magnetic atoms or molecules per unit volume</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer(s), $10^{-9}$ m</td>
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<td>isopropoxide</td>
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<tr>
<td>ppm</td>
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<tr>
<td>R$^2$</td>
<td>goodness-of-fit in linear regression</td>
</tr>
<tr>
<td>$\rho$</td>
<td>rho, density of material</td>
</tr>
<tr>
<td>s</td>
<td>second(s)</td>
</tr>
<tr>
<td>SAXS</td>
<td>small angle X-ray scattering</td>
</tr>
<tr>
<td>SI</td>
<td>International System of Units</td>
</tr>
<tr>
<td>SDBS</td>
<td>sodium dodecylbenzenesulfonate</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>sigma, induced magnetic moment per mass</td>
</tr>
<tr>
<td>sol-gel</td>
<td>synthetic process for producing solid material from small molecules</td>
</tr>
<tr>
<td>SQUID</td>
<td>superconducting quantum interference device</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>T</td>
<td>tesla</td>
</tr>
<tr>
<td>Tcf</td>
<td>trillion cubic feet</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>TREG</td>
<td>triethylene glycol</td>
</tr>
<tr>
<td>wt%</td>
<td>weight percent</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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XPS                  X-ray photoelectron spectroscopy
Introduction

For thousands of years, humans have been using petroleum and petroleum products for a wide variety of uses, spanning from wound dressings and laxatives to weapons of war to paving roads and sealing water works. As such, there has always been a large demand for petroleum and, eventually, other hydrocarbons. While oil seeps were plentiful across the world and rudimentary drilled was used, it wasn’t until the early 19th century that an increased need for oil was felt. Whale oil was becoming scarcer and the Industrial Revolution demanded a cheap source of lubricants and lighting oil. Meanwhile, the technology for drilling and obtaining oil was developed, leading to the first modern well being drilled in Pennsylvania, kicking off other wells across the United States and starting the petroleum industry.

The oil found in these early wells was often fairly close to the surface and in large reservoirs, usually in salt mines or near salt domes. It did not require as much effort or technology to capture this oil as it does to drill for oil currently; much of this oil seeped out of the ground during mining for salt and was considered a nuisance. However, as more and more wells were drilled, the easier to locate oil was drilled and pumped, forcing companies to start developing advancements in technology for both drilling and locating hydrocarbons. As drilling continued and the demand for oil and natural gas increased, hydrocarbons became easier to find, but harder to get out of the ground, especially in a way that was financially feasible. For instance, one of the largest quantities of hydrocarbons in the United States was found in shale plays all across the country, as seen in Figure I.1, but until recently it was difficult to remove the oil and gas that was trapped in the pores of the rock.

Shale is a sedimentary rock that is often found near reservoirs as a capping rock, helping to keep the oil contained in the reservoir. The reason it can do this so well is that
although it is highly porous and thus holds a lot of oil or natural gas, it is not very
permeable and so the oil cannot seep through to pool. When a conventional well is
drilled, the hydrocarbons pool in the well bore and the high pressure that exists in a well
pushes the hydrocarbons to the surface, but the oil trapped in the pores of shale were
impossible to collect efficiently as they cannot seep out of the rock into the well. It
wasn’t until 1947 that the method of hydraulic fracturing was developed and it was
several more decades until it became financially feasible.\footnote{7}

Hydraulic fracturing is a method often used to stimulate wells, particularly those
drilled into shale. A representation of the hydraulic fracturing procedure is depicted in
Figure I.2. Hydraulic fracturing works through the use of a high pressure liquid, proppant
(sand or ceramic, usually), and chemicals designed to aid in the fracturing process as a
means of fracturing the hydrocarbon-rich, impermeable, porous rock in order to allow the
hydrocarbons trapped to flow into the wellbore. After the fractures have been made, the

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure1.png}
\caption{A map of the shale plays across the 48 continuous States.}
\end{figure}
liquid and chemicals are removed, but the proppants remain behind to keep the fractures propped open. The fluid then placed into either trucks, which transport the fluid to a treatment facility or is pumped into retention pits for further treatment.

![Schematic of the hydraulic fracturing process.](image)

**Figure 1.2.** Schematic of the hydraulic fracturing process.

It is important that the high pressure liquid, often water, is at a pressure higher than the fracture gradient of the target rock in order to create the necessary fractures. Due to this, millions of gallons of water are used, along with tons of added chemicals and proppants. When cost for this quantity of water is combined with the fact that, if uncontrolled, more than 70% of the injected water can be lost in fracturing fluid leakoff through permeable rock thus requiring more water, as well as the costs for the equipment to handle high pressures, and the cost of managing flowback and produced water along with other technological considerations, hydraulic fracturing can cost a company anywhere between $400,000 to $2.5 million in fracking costs alone, with the full well cost being between nearly $600,000 to $10 million or more. Due to its
expensive nature, different techniques have been developed to ensure the fracking jobs are completely properly and efficiently for the best recovery of hydrocarbon and the highest economic return.$^{11,12}$

Some of the various types of measurements used for gaining information on the fractures include measuring the pressure in the well which has to be combined with the knowledge of the geology near the well,$^{13}$ microseismic monitoring,$^{14}$ and the use of radioactive tracers.$^{15,16}$ However, these methodologies have some drawbacks. For instance, the radioactive tracers are short-lived by design, which means there is a limited amount of time to take measurements as well as requiring a large quantity of material due to naturally occurring radioactive material in the surrounding rock. The use of microseismic monitoring or measuring of well pressure is limited by only being able to take measurements in two dimensions, whereas a series of fractures are three dimensional. This necessitates the use of a significant quantity of expensive and potentially toxic material or the combination of several methodologies, creating significant cost in addition to the cost of hydraulic fracturing and well production.

As the number of wells that undergo hydraulic fracturing increases each year, there is a growing number of claims of fracked wells leaking or otherwise contaminating the environment and eventually contaminating drinking water of the surrounding communities.$^{8,17,18}$ There have been reports of raised levels of methane in surface water as well as in drinking water, along with high levels of toxic compounds and other chemicals used in the fracking process. These contaminants can come from a variety of sources, including flowback or produced water overflowing or seeping into the near-surface environment, frack fluid leakoff, surface spills, improperly built or maintained waste pits, and improperly cased wells.$^{8,17,19,20}$

To combat this, there have been a number of methods developed to trace the fracking fluid or contaminations associated with fracking, including trace isotope analysis in both water$^{21}$ and methane.$^{22,23}$ With regards to methane, analysis is done on the $^{13}$C
isotope ratios as well as the ratio of methane to higher-chain hydrocarbons and the concentration of methane in the ground or drinking water. The results of these studies can be used to indicate if the methane detected is biogenic or mixed biogenic and thermogenic versus purely thermogenic. This then indicates if the methane naturally seeped into the water or if it was a contamination from a fractured well; the more thermogenic and the higher the quantity of higher-chain hydrocarbons, the more likely the methane increase is due to nearby hydraulic fracturing. Trace isotope analysis in water works in a similar fashion. This type of analysis analyzes the quantities of isotopes of boron and lithium that are typically found in shale formations. If a raised level of these isotopes is found in surface water, the assumption can be made that there is contamination from the well coming from some part of the fracking procedure. Furthermore, different quantities of these isotopes are found in different sources of wastewater, allowing for a finger printing and delineation of the contaminated water. By using this method, researchers hope to be able to pinpoint what part of the well the contamination is coming from.

Despite the success of these methodologies, both for tracing fractures in wells and tracing contamination sources, they all have drawbacks and limitations. Firstly, as was mentioned above, the quantity of water that is not only in the flowback, but also produced from the well is millions of gallons. In order to be able to detect the required signals for the above methodologies, the quantity of material required would be significant. Depending on the quantity required and the economic production of the well, this could become cost-prohibitive. This is on top of the potential cost of having to use multiple information gathering techniques as was discussed above. Secondly, while detection of trace isotopes in methane will determine if the methane is biogenic or thermogenic, it does not definitely determine if the methane is from a natural leak that was only brought to light because of the nearby fracking. Additionally, it cannot detect if there is contamination from fracking fluid. Finally, although the detection of trace isotopes in
water has the ability to allow for distinction between wastewater sources, it cannot be used to pinpoint which specific well is problematic, forcing the entire field to be inspected. This would require the shut-down of production until the source of the leak is found, which will cost companies millions of dollars.\textsuperscript{12}

In order to address the need for more information gathering in the well as well as addressing the concerns of environmental contamination, combined with the need for a non-toxic and easily detectable tracer, a new material would be required. When coming up with potential new materials, different techniques from various unrelated fields that, in essence, do something similar to what is desired were analyzed. One technique, and material in particular, stood out.

In the medical field, magnetic resonance imaging (MRI) is used as a means of medical diagnosis without invasive surgeries or ionizing radiations.\textsuperscript{24} An MRI works by creating a strong magnetic field around the subject or area of study and, through rapid variance of the magnetic field, detects the rate at which excited atoms, often hydrogen in water, return to equilibrium. Different tissues appear to be different shades, allowing for tissue and tissue anomalies to be imaged,\textsuperscript{25} diseases, such as heart, brain, or liver diseases to be diagnosed,\textsuperscript{25,26} bones to be imaged and analyzed for disease or anomalies,\textsuperscript{27} or even brain activity.\textsuperscript{28} However, it is a known problem that some tissues are similar enough in environment and water content to make it difficult to find or distinguish between two unique sets of tissues, such as a tumor in an organ.\textsuperscript{28} In order to overcome this, some sort of contrast agent is used. Often, the tracers are either highly magnetic or have a high magnetic susceptibility, which changes the relaxation time of the atoms that are in close proximity.\textsuperscript{28} These contrast agents are often administered intravenously.\textsuperscript{29}

Although there are many different types of contrast agents used in MRI, such as gadolinium or gadolinium containing contrast agents,\textsuperscript{30} I decided to focus on a contrast agent that has also been studied extensively: nanoscale magnetite.\textsuperscript{31-34} Magnetite has a low toxicity\textsuperscript{35} and is a very common mineral,\textsuperscript{24} making it ideal for tracing environmental
contaminations as it will not pose its own environmental threat and can be made cheaply.\textsuperscript{36,37} When magnetite is made at the nanoscale, it goes from being ferrimagnetic to superparamagnetic,\textsuperscript{38} allowing for the exploration of a wide range of magnetic properties and changes therein. Additionally, the size and shape of nanoparticles can be easily controlled via synthetic procedure.\textsuperscript{39-42} As size and shape of the nanoparticle can have a direct influence on the magnetic properties of the nanoparticle,\textsuperscript{41,43,44} this would give the ability to create a material with a specific and desired magnetic property that could be finely tuned for detection. The coating on the nanoparticle can also be altered to fit the situation as needed.\textsuperscript{45} The ability to modify the material to suit the needs required makes nanoscale magnetite incredibly versatile.

However, there are still drawbacks on being able to use magnetite as a tracer in wells. Firstly, syntheses that create water-soluble magnetite often has low control over size and/or shape of the nanoparticle.\textsuperscript{33} As was stated above, the size and shape directly affect that magnetic properties exhibited, with the larger the nanoparticle and more irregularly shaped leading to a decrease in magnetism. If the nanoparticles are not spherical, there is an increase in surface anisotropy, which decreases the magnetization.\textsuperscript{41} Additionally, if a nanoparticle is too large, the magnetization decreases due to conflicting magnetic domains and surface anisotropy.\textsuperscript{43,44} There is also a dependence of magnetic properties on temperature; as temperature increases, magnetic properties decrease.\textsuperscript{24} This is due to the fact that as temperature rises, the energy input into the system increases. This increase in energy input allows the spins inside a magnetic domain to flip randomly and thus cancel each other out. The higher the temperature, the greater the randomization of the spin until there is a net zero spin and the material becomes paramagnetic instead of ferri- or ferromagnetic. This point is called the Curie or Néel temperature, depending on whether the material was ferro- or ferrimagnetic, respectively. The Curie, or Néel, temperature can also be changed as a function of nanoparticle size and
composition,\textsuperscript{43,44,46,47} which in turn has an effect on the magnetic properties displayed at specific temperatures.

Conditions found in a well are also something that needs to be taken into consideration. First, the nanoparticle must be protected with a water-soluble surfactant, as it must be suspended in water and not react with the other chemicals used in hydraulic fracturing fluid. Additionally, it must be protected from the chemicals found naturally in wells, such as hydrogen sulfide. Hydrogen sulfide is known to react with magnetite to form iron(II) persulfide, which will change the magnetic properties of the starting nanomaterial.\textsuperscript{48,49} While this is useful as a hydrogen sulfide scavenger or as a means of detecting hydrogen sulfide, it is not beneficial for the tracing of fractures as, ideally, the magnetic properties, and thus the signal, should remain the same throughout the lifetime of the material.

The largest immediate drawback to using magnetization of nanoscale magnetite as a means of tracing and imaging hydraulic fractures is that the material will be used in a well that is surrounded by magnetic rock.\textsuperscript{50-52} Shale is known to contain minerals that are equally as magnetic as nanoscale magnetite.\textsuperscript{53} In order to overcome this background noise, there would be a need for a large quantity of material.\textsuperscript{37} It is possible to buy nanoscale magnetite in relatively large quantities, as it is produced commercially, but does not have as high of a magnetization, a small size or shape distribution, or is as protected as lab-synthesized magnetite, meaning it would require extra steps to make the material useable.\textsuperscript{54,55} In order to overcome this drawback, a different magnetic property would be required.

Magnetic susceptibility ($\chi$) is a constant that indicates the degree of magnetization of a material that has an external magnetic field applied to it.\textsuperscript{24} It is the ratio between the magnetization of the material ($M$) and the magnetic field strength ($H$) applied to it, as seen in equation I.1.

$$M = \chi H$$  \hspace{1cm} (I.1)
In order to be able to compare magnetic susceptibility across a wide range of materials, there are two different ways to report magnetic susceptibility: volume susceptibility and mass or molar susceptibility. In this report, mass magnetic susceptibility ($\chi_{\text{mass}}$) is reported.

Two of the largest benefits of using magnetic susceptibility instead of magnetization when using nanoscale magnetite as a tracer include magnetic susceptibility not being as temperature dependent as other magnetic properties and that nanoparticles can be superparamagnetic, which means that they have a very high magnetic susceptibility in large quantities.\textsuperscript{24} This increase in magnetic susceptibility will increase the signal-to-noise ratio against the background magnetization and magnetic susceptibility which in turn will mean there is less material needed in order to receive a distinguishable signal. Another

![Diagram of magnetization](image.png)

**Figure I.3.** Plot of magnetization ($M$) of a superparamagnetic material as a function of magnetic field strength ($H$). Magnetic saturation ($M_s$) is found at large magnetic field strength. Magnetic susceptibility is the slope of the line that is circled. At small $H$, this is very large.
added benefit of using magnetic susceptibility as opposed to magnetization is the field at which magnetic susceptibility is the greatest; the largest magnetic susceptibility signal for a material is often found at low magnetic fields as opposed to high magnetic fields for magnetization (Figure I.3). There have been low field producers and detectors that have been developed for analysis of cores in order to gain more insight into the geology surrounding the well;\textsuperscript{50} such technology is easily adapted for use of nanoparticles as tracers.

In addition to using magnetic susceptibility instead of magnetization, there are a few synthetic issues to address when synthesizing the nanoparticles. The first issue to address is the type of synthetic procedure used. There are several different synthetic methods to make nanoparticles, including milling, co-precipitation, microemulsion, hydrothermal, and thermal decomposition, amongst others.\textsuperscript{45} Milling nanoparticles requires large pieces of equipment for milling and can take hours to days to complete, but can be run in ambient conditions.\textsuperscript{33} The longer the milling time, the more pure the sample as well as the better size control,\textsuperscript{56} though there is little shape control as well as aggregation control, due to a lack of surfactant.\textsuperscript{33,57} Additionally, there is a chance of contamination from the equipment used,\textsuperscript{58} making it difficult to control composition. Co-precipitation syntheses also run in ambient conditions, but often require heating.\textsuperscript{33,44,45} Syntheses only take minutes and have a good size distribution as well as use water as a solvent, but do not have good shape control.\textsuperscript{33} Microemulsion syntheses are run in ambient conditions as well, with little heating, but take hours instead of minutes as compared to co-precipitation methods.\textsuperscript{33,59} The method yields nanoparticles with good size and shape control, but with a small yield.\textsuperscript{33} Hydrothermal syntheses require high pressure vessels and high temperatures.\textsuperscript{33,45} Each synthesis can take hours or days to complete, but are often run in a polar solvent, making the resulting nanoparticles water soluble.\textsuperscript{33} The size and shape distribution is good, but only has a fair yield.\textsuperscript{60,61} Out of all of the types of syntheses, thermal decomposition has the highest level of control over size...
and shape of the nanoparticles with a very high yield, but often requires high temperatures in an inert atmosphere and can take hours to days to complete.\textsuperscript{33,42,45,62} However, thermal decomposition syntheses are easily scalable to industrial levels\textsuperscript{63} and can have cheaper starting materials used to make nanoparticles of the same quality as expensive starting materials,\textsuperscript{36} making it the ideal synthesis to use.

An added benefit of starting with a thermal decomposition reaction and nanoscale magnetite is the ability to substitute in different metals in order to change magnetic properties of the nanoparticles. Various metal ferrites have been studied for a wide range of uses, all taking advantage of the changes in magnetic properties.\textsuperscript{62,64-66} The quantities of metals substituted into the crystal structure of magnetite have also been studied.\textsuperscript{42,46,67} Having the capability of altering the composition of the nanoparticles is beneficial because nanoparticles with distinct magnetic susceptibility and magnetization signals can be synthesized. These distinct signals can be used as a means of identification of wells that might be leaking or contaminating the environment. One of the larger issues to explore is the reproducibility and control over the composition, especially on large scales.

Large quantities of the nanoparticles will be necessary to synthesize, regardless of the strength of the signal, due to the large quantities of water used in hydraulic fracturing. A typical hydraulic fracture job uses 2 million to 4 million gallons of water.\textsuperscript{13} Depending on the magnetic properties of the surrounding rock, there could be a requirement for tens to hundreds of tons of material added to the frack water.\textsuperscript{37} Knowing the magnetic characterization of the shale surrounding the well is highly important in addition to knowing how easily the nanoparticles are detected against the shale and proppant used in the fracturing process. In addition, the distance the signal propagates also needs to be investigated.

Of course, as was stated earlier, hydraulically fractured wells are hot, usually 120 - 150 °C\textsuperscript{68,69} and since magnetic properties are known to decrease as temperature increases,\textsuperscript{24} the dependence of magnetic susceptibility and magnetization on temperature
needs to be studied and characterized. Additionally, the dependence of magnetic susceptibility and magnetization on composition needs to be characterized, especially as temperature increases. It is highly likely that different compositions will have different amounts of temperature dependence due to the change in spins and surface interactions of the substituted atoms in the lattice.\textsuperscript{46,66,67}

Finally, as was touched upon earlier, there is a requirement for the scalability of the synthetic method used to create the nanoparticles of choice. Different synthetic methods are known to produce different magnetic properties in nanoparticles of the same composition, so there needs to be an ability to control for that.\textsuperscript{46} A variety of scalable syntheses will be compared and the synthesis with the best control over composition, size, and shape that also has the least waste, highest yield, and least amount of cost will be investigated further.

Additionally, in order to be able to detect the nanoparticles, there needs to be a method developed to remove the nanoparticles from the environment. Even though the quantity of nanoparticles required for detection can be determined,\textsuperscript{37} detection could require tons of material. In order to reduce the quantity of material required, a methodology for concentrating and removing nanoparticles from water in an efficient manner needs to be developed. Once all of these different issues are addressed and resolved, the ideal magnetic nanoparticle for use in hydraulically fractured wells will be able to be synthesized in large quantities for industrial use.

References


Chapter 1

Reagent control over the composition of mixed metal ferrite nanoparticles

Portions of this chapter are included in A. W. Orbaek, L. Morrow, S. J. Maguire-Boyle, A. R. Barron, *J. Exp. Nanosci.*, 2013, DOI:10.1080/17458080.2013.832422. A reprint can be found in Appendix B. A full publication list can be found in Appendix A.

Introduction

As a consequence of their potential applications as contrast agents, tracers, energetic materials, and catalysts, there here has been extensive research towards the synthesis of nearly monodisperse metallic and metal oxide nanoparticles (NPs). In the majority of applications control over the size and size distribution are important considerations; however, where mixed metal ferrites are desired the control over the atomic composition is also a factor. Recently, there has been an increase in interest in the potential use of superparamagnetic NPs as tracers in geological formations. The idea being that variation in the magnetic susceptibility can be used as a method for differentiating one tracer from another and from naturally occurring background materials.

Common synthetic routes for the preparation of narrowly disperse metallic and mixed metal ferrite NPs include co-precipitation of metals salts, hydrolysis of metal salts (e.g., sol-gel), thermal decomposition of organometallic precursors, or the polyol process. Of these methods the thermal decomposition of organometallic precursors in non-coordinating, high boiling organic solvents in the presence of templating/surface capping ligands has proven to be a flexible method for polymetallic nanoparticles with decent control over size and distributions.
Nanoparticle synthesis in non-coordinating solvents was originally developed for the synthesis of semiconductor nanocrystals,\textsuperscript{7} based on the concept of providing reactive substituents to both components of the system,\textsuperscript{8,9} however, recently it has become an attractive method for producing metallic and mixed metal ferrite NPs, e.g., via the one-pot synthesis of bimetallic ferrite NPs by the thermal decomposition of metal acetylacetonate (acac) precursors in high boiling ethers.\textsuperscript{10,11}

It has been previously reported that for the composition of cobalt ferrite nanoparticles (i.e., Co:Fe ratio), as synthesized from the appropriate metal acac precursors, the Co concentration increase linearly with increasing Co(acac)\textsubscript{2} precursor concentration, and only a very small percentage of Co(acac)\textsubscript{2} was not directly incorporated into the NPs.\textsuperscript{12} This suggested that the kinetics of the decomposition of each precursor [Fe(acac)\textsubscript{3} and Co(acac)\textsubscript{2}] is near identical and that the composition of the NPs is statistically a function of the starting precursor mixture. In the course of our studies we have become interested in whether compositional control can be extended to other systems and what factors of the precursor stability, structure, reactivity control the composition of the final nanoparticle. Our initial results in this area are described herein.

\textbf{Results and Discussion}

As noted in the introduction, it has been previously reported that the composition of cobalt ferrite nanoparticles (i.e., Fe:Co ratio) prepared by the thermal decomposition in benzyl ether of Fe(acac)\textsubscript{3} and Co(acac)\textsubscript{2}, in the presence of a mixture of oleic acid and oleylamine surface capping ligands, and 1,2-hexadecanediol (HDD) as an accelerating agent, is directly related to the composition of the metals in the precursor solution. However, the size and size distribution of the NPs was found to depend on the relative concentration of oleic acid, oleylamine, HDD, and the metal precursor. In order to investigate the effect of reactant composition (M:M') we have maintained the relative concentration of each reactant, including the total concentration of the metal precursors.
Thus, mixed metal ferrite nanoparticles (M-Fe-O and M-M'-Fe-O) have been prepared using the appropriate M(acac)$_n$ precursors. The elemental composition of the isolated NPs has been determined by inductively coupled plasma – optical emission spectroscopy (ICP-OES), while the particles sizes have been measured by small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) measurements.

The choice of the particular mixed metal compositions has been dictated by the desire to gain information on the uniformity of NP compositions for tracer applications. Ideally, the NPs would be used for down-hole sensors for the oil and gas industry, in which the temperature dependent low field magnetic susceptibility is used as an identification tool. Small changes in composition will have a large change in the magnetic susceptibility. In this regard, the MnZn ferrite and AlGd ferrite compositions are of interest.

**Mn ferrite NPs.** shows the composition of Mn ferrite NPs, as determined by ICP-OES, prepared from various solutions of Fe(acac)$_3$ and Mn(acac)$_2$ (Table 1.1). Although the Mn concentration generally increases with increasing Mn(acac)$_2$ precursor concentration (Figure 1.1, circles) less Mn is incorporated into the nanoparticles (see difference between circles and dashed lines in Figure 1.1).

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**Figure 1.1.** Atomic percentage of manganese incorporated into Mn ferrite NPs versus the amount Mn(acac)$_2$ used in the reaction. The ideal ratio is shown as a dashed line while the dotted line is the linear fit.

It should be recognized that ICP-OES analysis provides an average composition of the isolated nanoparticles. At the extreme case ICP-OES does not differentiate between samples of nanoparticles that are solid solutions (i.e., Mn ferrite nanoparticles) versus a mixture of nanoparticles of different compositions (i.e., Fe-O and Mn-O nanoparticles). While it is also possible for composition to vary within individual particles,\textsuperscript{13} it is more logical to study the uniformity over a small range of nanoparticles. Orbaek, et al. used energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) to analyze the nanoparticles and showed at low Mn content there is a variation of composition across various areas analyzed.\textsuperscript{14} In addition, the values are lower than the bulk analysis obtained by ICP-OES. At higher Mn content there is a wider range
of values from EDX, but the average (40.2% Mn) is the same as the ICP-OES analysis (40.24% Mn). These results indicate that there is a range of Fe:Mn ratios between each Mn ferrite NP. While the ICP-OES analysis represents an average of the whole sample, individual particles can vary in composition as much as 30%.

The detailed mechanism of the synthesis of metal oxide nanoparticles from M(acac)_n precursors at high temperature in organic solvents is not understood as clearly as the equivalent synthesis under hydrolytic conditions. However, under the conditions used herein, there are two general mechanistic pathways that should be considered: 1) the direct thermal decomposition of the M(acac)_n precursor and 2) ligand exchange between the M(acac)_n and 1,2-hexadecanediol (Eq. 1.1) with the subsequent thermal decomposition of the alkoxide compound. The role of the oleic acid or oleylamine appear to be that of capping agents on the surface of the growing nanoparticle; however, their role in the decomposition of the precursors cannot be discounted.

\[
M(\text{acac})_n + \text{HO-R-OH} \rightarrow M(\text{acac})_{n-1}(\text{O-R-OH}) + \text{acac-H} \quad (1.1)
\]

In consideration of the first reaction pathway, the thermal decomposition temperature of Mn(acac)_2 (248 °C) is significantly higher than that of Fe(acac)_3 (184 °C) that would result in incorporation of Fe in preference to Mn, which is what is observed. With regard to ligand exchange it is difficult to find comparable data; however, a few general observation can be made. In the solid state Mn(acac)_2 exists as the hydrate, i.e., Mn(acac)_2·(H_2O)_2, with Jahn-Teller distorted octahedral geometry as a consequence of its d^5 valence state. It is expected that in the present reaction that this geometry will be maintained in solution, albeit with solvent (benzyl ether) or an appropriate ligands (oleic acid or oleylamine or HDD) as axial ligands. Fe(acac)_3 also has a Jahn-Teller distorted octahedral geometry. While the presence of three chelate ligands may be expected to stabilize the complex with regard to ligand exchange, ligand exchange for Fe(acac)_3 is
significantly faster than for other M(acac)$_3$ complexes.$^{18}$ Thus, the preferential incorporation of Fe over Mn is expected based upon the mechanisms understood to occur for M(acac)$_n$ formation of M-O nanoparticles.

**Figure 1.2.** Dependence of Mn ferrite NP size as a function of the metal precursor concentration. The dotted line is the fit.

**Figure 1.3.** TEM images of Mn ferrite NPs prepared from Fe(acac)$_3$:Mn(acac)$_2$ ratio of (a) 2:1 (sample 1.1) and (b) 1:1 (sample 1.2). Scale bar is 50 nm for each.
As shown in Figure 1.2, the Mn ferrite nanoparticle diameters and distributions, as measured by SAXS, are relatively constant (within particle size distribution) as a function of either the reaction composition or the composition of the isolated nanoparticles. The SAXS data is in agreement with TEM data (e.g., Figure 1.3a-b), which gives sizes for the nanoparticles in samples 1.1 and 1.2 as 9.1±1.5 nm and 8.4±1.1 nm, respectively.

**Zn ferrite NPs.** Figure 1.3 shows that the composition of Zn ferrite NPs, as determined by ICP-OES. Similar to what is observed with Mn ferrite NPs, the amount of Zn that is incorporated into Zn ferrite NPs increases as the initial Zn(acac)$_2$ precursor increases (Figure 1.4, circles). However, much like Mn ferrite NPs, less Zn is incorporated into the nanoparticles than is expected (the difference between the dashed line and the circles in Figure 1.4).

![Graph](image.png)

**Figure 1.4.** Atomic percentage of zinc incorporated into Zn ferrite NPs versus the amount Zn(acac)$_2$ used in the reaction. The ideal ratio is shown as a dashed line while the dotted line is the linear fit.
The size of the nanoparticles was characterized as well, via SAXS and TEM. SAXS gives the diameter of the nanoparticles to be 12 nm ±4 nm (Figure 1.5). TEM, on the other hand, gives the diameter of the nanoparticles to be 17 ±2 nm (a representative sample can be seen).

**Figure 1.5.** Dependence of Zn ferrite NP size as a function of the metal precursor concentration.

**Figure 1.6.** A representative TEM image of Zn ferrite NPs prepared from Fe(acac)₃:Zn(acac)₂ ratio of 2:1 (sample 1.4). Scale bar is 50 nm.
in Figure 1.6). Although close, there is a discrepancy between the two analytical techniques. This could be due to the analysis of the particle size in SAXS. In the program used, NANO-Solver, the nanoparticles can be analyzed as spherical or core-shell model, amongst others. It is known that the different models can often report slightly different sizes. The core-shell model was attempted; it did not fit the particles and would consistently give errors and so the spherical model was the one used for analysis.

**Al ferrite NPs.** The choice of a precursor with a very high thermal stability should force its incorporation into a NP to be as a function of ligand exchange, and thus allow for a comparison of the two processes. Al(acac)$_3$ is thermally stable (257 °C) and undergoes ligand exchange slowly compared to Fe(acac)$_3$.\textsuperscript{18,19}

![Graph showing Al in nanoparticle (%) vs Al(acac)$_3$ (%)](image)

**Figure 1.7.** Atomic percentage of aluminum incorporated into Al ferrite NPs versus the amount Al(acac)$_3$ used in the reaction. The ideal ratio is shown as a dashed line.

The attempt at synthesizing Al ferrite nanoparticles using Fe(acac)$_3$ and Al(acac)$_3$ showed less Al incorporated into the nanoparticles that expected. In fact, at very low Al:Fe ratios the majority of samples had essentially no Al incorporated, while above an
Al:Fe ratio of 0.5 the Al content reaches a maximum of 17%. Increasing the amount of Al(acac)₃ in the reaction mixture results in less Al being incorporated into the NPs (see Figure 1.7).

The size and size distribution of the Al ferrite NPs were determined SAXS. As may be seen from Figure 1.8 the average size shows a general trend of increasing with decreased iron content in the reaction mixture. Given the low levels of aluminum incorporated in the final nanoparticles, this is consistent with prior results where a decreased metal precursor concentration results in larger nanoparticles. Thus, it appears that the presence of the low reactive Al(acac)₃ behaves almost as a diluent in the formation of ferrite nanoparticles. Thus, at high Al(acac)₃ concentrations in the reaction mixture, the size of the nanoparticles formed is similar to that of simply reducing the “active” precursor concentration and hence the seed formation rate.

![Figure 1.8](image)

**Figure 1.8.** Dependence of Al ferrite NP size as a function of the metal precursor concentration. It should be noted the error bars are present on all data.

As expected with minimal Al incorporated into the nanoparticles, TEM images (Figure 1.9) show little change in the size or shape of the particles. Furthermore, d-
spacing from high resolution TEM images are within experimental error of those expected for magnetite (Fe-O) nanoparticles (8.39 Å).

![Typical TEM image of Al ferrite NPs with high resolution TEM image of an individual particle inset.](image)

**Figure 1.9.** Typical TEM image of Al ferrite NPs with high resolution TEM image of an individual particle inset.

Given the high thermal stability and low rate of ligand exchange observed for Al(acac)$_3$ it is unsurprising that there is only minimal incorporation into the Al ferrite NPs. If ligand exchange (Eq. 1.1) is valid pathway, and the product of such an exchange would be a metal alkoxide, then the use of an alkoxide precursor (with known ability to form the appropriate metal oxide) should enhance the incorporation of the metal into the NPs. In this regard, aluminium alkoxides are well known as precursors for alumina nanoparticles.$^{15,22}$ We therefore investigated the synthesis of Al ferrite NPs using mixtures of Fe(acac)$_3$ and Al(OiPr)$_3$. 
Figure 1.10 shows the composition of Al ferrite NPs prepared from solutions of Fe(acac)$_3$ and Al(O$^i$Pr)$_3$. The Al concentration increase with increasing Al(O$^i$Pr)$_3$ precursor concentration and follows the ideal relationship (dashed line) closer than observed for the Mn ferrite NPs. Furthermore, unlike the reactions with Al(acac)$_3$ (see Figure 1.7) high Al:Fe ratios can be achieved.

![Figure 1.10](image)

**Figure 1.10.** Atomic percentage of aluminum incorporated into Al ferrite NPs versus the amount Al(O$^i$Pr)$_3$ used in the reaction. The ideal ratio is shown as a dashed line.

As noted above, the decomposition temperature and ligand exchange of Al(acac)$_3$ as compared to Fe(acac)$_3$ make it impossible to create Al ferrite NPs with high Al content, irrespective of the relative concentrations of the precursors in the reaction mixture. However, if an alternative Al precursor is employed that undergoes ligand exchange readily the result appears to be more comparable kinetics of decomposition under the present conditions, i.e., $k[\text{Fe(acac)}_3] \approx k[\text{Al(O}^i\text{Pr)}_3]$. 

**Gd ferrite NPs.** In the examples studied above, although the uniformity in composition of individual NP may vary, the ICP-OES analysis of multiple samples prepared with the same reagent composition are within experimental error.$^{13}$ Thus, the
reproducibility of the reactions is high, allowing for predictability once the relationship between reagent composition and NP analysis is understood. However, during these studies, it was determined that such reproducibility is not the case for the synthesis of Gd ferrite NPs.

**Figure 1.11.** Atomic percentage of gadolinium incorporated into Gd ferrite NPs versus the amount Gd(acac)$_3$ used in the reaction. The ideal ratio is shown as a dashed line. The use of open squares allows for repetitive analysis of the same sample.

Figure 1.11 shows the composition of composition of Gd ferrite NPs prepared from solutions of Fe(acac)$_3$ and Gd(acac)$_3$. While the gadolinium concentration in the isolated nanoparticles generally increases with increasing Gd(acac)$_3$ precursor concentration and straddles the ideal relationship (Figure 1.11, dashed line), unlike the Mn ferrite system, there appears to be no clear trend to allow the prediction of the composition of the final nanoparticles from the reaction mixture. The thermal decomposition temperature of the Gd(acac)$_3$ (143 °C) is slightly lower than that of Fe(acac)$_3$ (184 °C), which would be expected to result in the preferential incorporation of
Gd over Fe; while this is not observed for the binary (Gd ferrite) NPs it is observed for the ternary (AlGd ferrite) NPs, see below.

Initially, the poor correlation was assumed to be an issue with either the ICP-OES standards and or the digestion process. Consequently, several samples were re-analysed using freshly prepared calibration solutions and with increased digestion times. Table 1.2 and Figure 1.11 shows that irrespective of the ICP-OES protocol the compositional analysis remain within ca. 5%. However, repeating reactions multiple times gave different Gd:Fe ratios, e.g., 50% Gd (Figure 1.11 and Table 1.2). This suggests that while the analysis is accurate and representative, the composition depends on both the reagent ratio and other factors. In order to explore these variations reactions were performed using the same precursor (and reagent) ratios but different reaction sequences.

<table>
<thead>
<tr>
<th>Gd(acac)$_3$ (%)</th>
<th>Gd composition from ICP-OES (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.33</td>
<td>25.06, 25.39, 26.66</td>
</tr>
<tr>
<td>40.00</td>
<td>26.09, 27.32</td>
</tr>
<tr>
<td>50.00</td>
<td>70.25, 71.06, 72.18</td>
</tr>
<tr>
<td>50.00</td>
<td>15.51, 14.80, 14.74</td>
</tr>
<tr>
<td>60.24</td>
<td>14.17, 15.05, 16.26</td>
</tr>
<tr>
<td>66.67</td>
<td>15.93, 14.74</td>
</tr>
<tr>
<td>70.00</td>
<td>62.83, 64.01, 64.06</td>
</tr>
<tr>
<td>80.00</td>
<td>67.82, 68.69, 70.77</td>
</tr>
</tbody>
</table>

Two batches of Gd ferrite NPs (sample 1.23) were prepared with different reaction protocols. In one version the solvent was preheated to 200 °C, the metals, HDD,
oleic acid, and oleylamine were mixed separately and added. In a second route, the solvent and the metal complexes were preheated to 200 °C and then the oleic acid and oleylamine were subsequently added. In each of these cases the Gd analysis was 5.30% and 5.90%, respectively, as compared to 15.03% when all the reagents are heated together. This suggests that for the Gd ferrite system the composition of the resulting nanoparticles are very dependent on the small variations in the reaction conditions, e.g., rate of heating, mixing rates, etc.

![Graph](image)

**Figure 1.12.** Dependence of Gd ferrite NP size as a function of the metal precursor concentration.

The size and size distribution of the Gd ferrite NPs were determined SAXS. As may be seen from Figure 1.12 the average size ranges from 5 to 7 nm for reactions mixtures with an Fe:Gd < 0.6. At higher Gd concentrations the size shows a general trend of increasing with decreased iron content. A comparison of the size as a function of Gd in the reaction mixture or the isolated nanoparticles shows that the particle size is controlled by the reaction composition rather that the product composition.
It should be noted that Gd ferrite NPs have recently been shown to be effective for tumor therapy via magnetic field hyperthermia.\textsuperscript{24} However, in this case the Gd composition was $<1\%$, and the synthesis was with the appropriate chlorides ($\text{FeCl}_3$, $\text{FeCl}_2$, and $\text{GdCl}_3$) in an aqueous sol-gel reaction.

**MnZn ferrite NPs.** For ternary oxide mixtures the issue of compositional control is further complicated. Mixed ferrites have been previously reported with using $\text{MnCl}_2$, $\text{ZnSO}_4$ and $\text{FeCl}_3$ as the precursors.\textsuperscript{25} As with this prior work the iron precursor concentration was maintained constant, while the relative amounts of the Mn and Zn precursors [$\text{Mn(acac)}_2$ and $\text{Zn(acac)}_2$, respectively] were varied, see Table 1.3. As may be seen from the data in Figure 1.13 the composition of the resulting nanoparticles, as

![Figure 1.13](image)

**Figure 1.13.** The ratio of Mn:Zn incorporated into MnZn ferrite NPs as determined by ICP-OES versus the ratio of $\text{Mn(acac)}_2$:Zn(acac)$\textsubscript{2}$ used in the reaction ($R^2 = 0.964$). Ideal ratio is shown as a dashed line.

measured by the Mn:Zn ratio, closely follows the ratio of the precursors. Thus, allowing for the reproducible synthesis of NPs with desired composition. Furthermore, this suggest that the relative reaction rates of Mn(acac)$_2$ and Zn(acac)$_2$ are similar despite differences
in thermal stability (248 °C versus 135-138 °C, respectively). Zn(acac)$_2$ is only a monomer in the vapour phase, and is a trimer in the solid state, i.e., Zn$_3$(acac)$_6$, in which each Zn ion is coordinated by five oxygen atoms in a distorted trigonal bipyramid structure.$^{26,27}$ It is therefore interesting that despite different thermal stability and differences in structure that would be expected to alter the relative reactivity, the incorporation of Mn and Zn is predictable.

Table 1.3. Summary of metal precursor composition for ternary mixed metal ferrite NPs.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Fe(acac)$_3$ (mmol)</th>
<th>Mn(acac)$_2$ (mmol)</th>
<th>Zn(acac)$_2$ (mmol)</th>
<th>Al(acac)$_3$ (mmol)</th>
<th>Gd(acac)$_3$ (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.33</td>
<td>2.00</td>
<td>0.65</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>2.00</td>
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<td>0.65</td>
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<tr>
<td>1.35</td>
<td>40.00</td>
<td>13.00</td>
<td>7.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.36</td>
<td>1.33</td>
<td>0.066</td>
<td>0.594</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.37</td>
<td>1.33</td>
<td>0.132</td>
<td>0.528</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.38</td>
<td>1.33</td>
<td>0.198</td>
<td>0.462</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.39</td>
<td>1.33</td>
<td>0.264</td>
<td>0.396</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.40</td>
<td>1.33</td>
<td>0.330</td>
<td>0.330</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.41</td>
<td>1.33</td>
<td>0.396</td>
<td>0.264</td>
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<tr>
<td>1.42</td>
<td>1.33</td>
<td>0.462</td>
<td>0.198</td>
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<tr>
<td>1.43</td>
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<td>0.528</td>
<td>0.132</td>
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<tr>
<td>1.44</td>
<td>1.33</td>
<td>0.594</td>
<td>0.066</td>
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<tr>
<td>1.45</td>
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<td>1.46</td>
<td>0.50</td>
<td>0.50</td>
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<tr>
<td>1.47</td>
<td>0.33</td>
<td>0.50</td>
<td>0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.48</td>
<td>0.25</td>
<td>0.50</td>
<td>0.50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The size and size distribution of the MnZn ferrite NPs were determined by SAXS for all the compositions prepared. As may be seen from Figure 1.14, the average size ranges from 6 to 8 nm; however, the variation is within the size distribution. Thus, the size of the nanoparticle shows no significant dependence on the relative ratio of manganese and zinc. This is further supported by TEM analysis of the NPs as shown in Figure 1.15. While the size and size distribution appear unaffected by the composition, the shape of the NPs appears less regular the higher the Mn content. This result is distinct from previous work by Arulmurugan et al. that showed for that the particle size decreased with increased Zn content. The X-ray diffraction (XRD) of samples 1.33, 1.38, 1.40, and 1.42 shows magnetite phase across all the composition (Figure 1.16). The crystalline domain sizes range from 59 Å (sample 1.33) to 123 Å (sample 1.38).

**Figure 1.14.** Dependence of MnZn ferrite NP size as a function of the ratio of Mn(acac)₂:Zn(acac)₂ used in the reaction.

**AlGd ferrite NPs.** Whereas the Mn and Zn precursors appear to be incorporated into nanoparticles, at an equal rate, investigation of a ternary mixture where the metals appear to show highly different rates is instructive. As discussed above, aluminium shows low
incorporation, while gadolinium is easily incorporated (albeit with a variability). Thus, the composition of AlGd ferrite nanoparticles was investigated. Figure 1.17 shows the Al:Fe:Gd composition of both the precursor solution (Table 1.4) and the nanoparticle composition. The plot shows that in all cases the nanoparticle composition is higher in Gd and lower in Al than expected from the reaction mixture. Furthermore, at low Fe(acac)₃ concentration the isolated nanoparticles appear to be Gd₂O₃.

Figure 1.15. Examples of typical TEM images of MnZn ferrite NP prepared using (a) Mn:Zn 0.9:0.1 and (b) Mn:Zn 0.2:0.8.

Figure 1.16. X-ray diffraction (XRD) of MnZn ferrite NP (sample 1.33).
**Figure 1.17.** The Al:Fe:Gd composition of the AlGd ferrite NPs as determined by ICP-OES (■) compared to the composition of the M(acac)$_n$ precursors used (□) in the reaction ($R^2 = 0.964$).

**Table 1.4.** Summary of compositional control for binary metal ferrite and ternary metal ferrite NP synthesis using Fe(acac)$_3$ as the iron precursor.

<table>
<thead>
<tr>
<th>Desired NP</th>
<th>Metal precursor</th>
<th>Compositional control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn ferrite</td>
<td>Mn(acac)$_2$</td>
<td>Yes</td>
</tr>
<tr>
<td>Zn ferrite</td>
<td>Zn(acac)$_2$</td>
<td>Yes</td>
</tr>
<tr>
<td>Al ferrite</td>
<td>Al(acac)$_3$</td>
<td>No</td>
</tr>
<tr>
<td>Al ferrite</td>
<td>Al(O$^i$Pr)$_3$</td>
<td>Yes</td>
</tr>
<tr>
<td>Gd ferrite</td>
<td>Gd(acac)$_3$</td>
<td>No</td>
</tr>
<tr>
<td>MnZn ferrite</td>
<td>Mn(acac)$_2$, Zn(acac)$_2$</td>
<td>Yes</td>
</tr>
<tr>
<td>AlGd ferrite</td>
<td>Al(acac)$_3$, Gd(acac)$_3$</td>
<td>No</td>
</tr>
</tbody>
</table>

The size and size distribution of selected AlGd ferrite NPs were determined by SAXS. The size increased (from 8 nm to 11 nm) with decreasing Fe content; however, the distribution remained constant (±2 nm).
Conclusions

The ability to control the composition (and compositional uniformity) of mixed metal oxide nanoparticles through the ratio of reagents in the reaction mixture was investigated. As may be seen from Table 1.4 there is compositional control for most of the nanoparticles; however, the predictability is not necessarily a direct correlation (ratio of reagents = ratio in NP). Instead once a calibration curve is obtained a specific desired composition can be attained. It appears that where the kinetics of decomposition of the various metal precursors is similar then a direct correlation is obtained (e.g., MnZn ferrite), however, where the reactivity is slightly different a deviation, albeit predictable, from ideal is observed (e.g., Mn ferrite). However, when the reaction rate for one precursor is vastly different from the other [e.g., Al(acac)₃ versus Fe(acac)₃] then alternative precursors [e.g., Al(OiPr)₃] must be used.

It is also important to note that since the particle size and shape may remain unchanged over a wide composition range, this cannot be used solely along with bulk analysis to ensure that the desired composition has been obtained across all the nanoparticles in the sample, i.e., homogeneity is not guaranteed because the overall composition is that desired. As such researchers should be cautioned in assuming uniform composition.

Experimental Methods

Materials. Fe(acac)₃ (97%), Al(acac)₃ (99%), Al(OiPr)₃ (≥98%), Gd(acac)₃·2(H₂O) (99.9%), Mn(acac)₂, and Zn(acac)₂·x(H₂O) hydrate, were obtained from Sigma Aldrich and used without further purification. Oleic acid [CH₃(CH₂)₇CH=CH(CH₂)₇CO₂H, 90%], oleylamine [CH₃(CH₂)₇CH=CH(CH₂)₈NH₂, >70%], 1,2-hexadecanediol [CH₃(CH₂)₁₃CH(OH)CH₂OH, HDD], benzyl ether (98%),
and hexanes (mixture of isomers) were all purchased from Aldrich and used as received. Ethanol (200 proof) from Decon Laboratories Inc. was used as received.

**Characterization.** Size determination of the nanoparticles was achieved by small angle X-ray scattering (SAXS) using a Rigaku SmartLab X-Ray diffractometer using a Cu-K\textsubscript{α} radiation source. Samples were prepared by sealing a concentrated nanoparticle solution in hexanes into a 1 mm “Glass Number 50 Capillary” tube (Hampton Research Inc.) and the data was resolved using Rigaku’s NANO-solver. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements were obtained on a Perkin Elmer Optima 4300DV. Samples were prepared by digesting 0.5 mL of concentrated nanoparticle solution in 9.5 mL of concentrated HNO\textsubscript{3}. 0.5 mL of the digested solution was diluted into 9.5 mL of NANOpure\textsuperscript{TM} water. ICP standards were obtained from inorganic adventures and diluted using NANOpure\textsuperscript{TM} water. The iron content was accumulated first for each set of particles, then the additional metal concentration was determined after, to avoid complications arising from emission wavelength overlap between the Fe and the additional metals. The X-ray diffraction (XRD) was collected using a Rigaku D/Max Ultima II diffractometer configured with a vertical theta/2-theta goniometer, Cu-K\textsubscript{α} radiation, graphite monochromator and scintillation counter. Samples were prepared by precipitating the NPs out of solution, and drying before grinding the sample into a fine powder with a mortar and pestle. A zero-background sample holder was used. The sample was placed on the holder with some putty and a thin glass wafer and was pressed using a clean microscope slide to ensure the sample was level with the edge of the sample holder.

**Nanoparticle synthesis.** The synthesis used for the binary and ternary oxide NPs is a thermal decomposition reaction.\textsuperscript{6,11,12} It is carried out in an oxygen-free three-necked round bottom flask. The overall ratio of metal (2 mmol) to surfactant was kept constant.
In the case of the MnZn ferrite nanoparticles the amount of iron was kept constant, while manganese and zinc amounts were varied. In a general synthesis, 1,2-hexadecanediol (2.58 g, 10.0 mmol), oleic acid (1.90 µL, 6.00 mmol), and oleylamine (1.97 µL, 6.00 mmol) in benzyl ether (20.0 mL, 103 mmol) was used for each run. When all chemicals were added argon was flushed through the system to remove any oxygen. The system was then heated to 200 °C at a rate of 10 °C/min. Once at 200 °C, heating was held constant for two hours. After two hours, heating was increased to reflux at the same rate of 10 °C/min. Once refluxing, heating was held constant for one hour. After one hour, heating was turned off and entire system was let cool to room temperature. Ethanol (40 mL) was added to the solution to precipitate out the nanoparticles. The solution was then split into 50 mL centrifuge tubes and centrifuged. The supernatant was discarded and ethanol (15 mL) was added to each tube to wash the nanoparticles. The samples were centrifuged and washed twice more, discarding the supernatant each time. After washing, the nanoparticles were allowed to air-dry overnight and then suspended in hexanes.

A modified synthesis was used to make Al ferrite binary oxide NPs. The synthesis is carried out in an oxygen-free three-necked round bottom flask. The overall ratio of metal (2 mmol) to surfactant was kept constant. The ratio of iron to aluminium was varied in such a way that both metals combined equals 2 mmol. In the general synthesis, 1,2-hexadecanediol (0.388 g, 1.50 mmol), oleic acid (951 µL, 3.00 mmol), and oleylamine (987 µL, 3.00 mmol) in benzyl ether (37.5 mL, 197 mmol) was used for each run. When all chemicals were added argon was flushed through the system to remove any oxygen. The system was then heated to 200 °C at a rate of 10 °C/min. Once at 200 °C, heating was held constant for two hours. After two hours, heating was increased to reflux at the same rate of 10 °C/min. Once refluxing, heating was held constant for one hour. After one hour, heating was turned off and entire system was let cool to room temperature. Ethanol (40 mL) was added to the solution to precipitate out the nanoparticles. The solution was then split into 50 mL centrifuge tubes and centrifuged.
The supernatant was discarded and ethanol (15 mL) was added to each tube to wash the nanoparticles. The samples were centrifuged and washed twice more, discarding the supernatant each time. After washing, the nanoparticles were allowed to air-dry overnight and then suspended in hexanes.

References


Chapter 2

Detection of magnetic nanoparticles against proppant and shale reservoir rocks

Portions of this chapter are included in L. Morrow, D. K. Potter, and A. R. Barron, *J. Exp. Nanosci.*, 2014, DOI:10.1080/17458080.2014.951412. A reprint can be found in Appendix C. A full publication list can be found in Appendix A.

Introduction

Shale gas represents the largest fraction of natural gas in the continental United States. With an estimated 482 trillion cubic feet (Tcf) of hydrocarbon,\(^1\) shale gas has the potential to be the primary energy source for power generation in the US for the coming decades.\(^2\)\(^-\)\(^4\) The ability to extract shale gas economically has been achieved by the use of horizontal drilling techniques and hydraulic fracturing. Hydraulic fracturing (also known as “fracing” or “fracking”) uses water, proppant (sand or ceramic particles), and chemicals, pumped at high pressures into the well bore, to induce fracturing of the shale, creating permeability so the gas can migrate into the well bore and to the surface.

In order to maximize the recovery of oil and gas it is important to obtain information on the extent of the fracture flow characteristics of the rock within the hydraulically fractured reservoir.\(^5\) Characterization has traditionally been accomplished using techniques such as seismic measurements and nuclear magnetic resonance well logging; however, these methods have limitations and new methods are being investigated, including: conductive polymers,\(^6\) active or passive devices,\(^7\) or proppant tracking materials.\(^8\) The low porosity and permeability of many oil and gas reservoirs even after hydraulic fracturing, means that any sensor or tracer material must have a size sufficiently small to allow for its transport through the fractured rock formation. Nanoparticles (NPs) offer potential because one can change the surface properties to
allow mobility\textsuperscript{9} and their core may have a range of properties that can be sensed or reported. As such, NPs represent a potential sensor/tracer material and a number of mechanisms have been suggested for detection.\textsuperscript{10}

There has been significant research into the use of magnetite as a tracer in biological applications, such as in magnetic resonance imaging (MRI), taking advantage of the magnetic properties of the nanoscale magnetite (nMag) in order to create a large contrast between the particles and the surrounding tissue.\textsuperscript{11-15} The non-toxic nature of nMag would also have an advantage on environmental grounds\textsuperscript{16} and so it has been proposed that it should be possible to scale up this technology to the size of a reservoir using magnetic nanoparticles and a large magnetic source and receiver.\textsuperscript{10} This approach has merit since it is already known that studying the magnetic anisotropy of the reservoir source rocks can give a good understanding of the characteristics and structure of such formations.\textsuperscript{17}

Given that the function of the proppant is to hold open the cracks that are formed in the source rock (shale) during the frac process, the presence of a nano sensor would be most likely associated with the proppant pack. Thus, it is important to ascertain if nMag may be distinguished from typical proppant materials. The most common proppant is high quartz sand such as the hydraulic fracturing sand (frac sand) used herein; however, due to the low crush strength of sand, ceramic particles are often used as proppant and so we have used a typical high density ceramic proppant (CarboHSP). In addition, since the resolution of the measurement will be lower than the size of the propped fractures (>300 nm depending on the size of the proppant particle), then, in order to differentiate the nMag from the background rock, the concentration of nMag must be sufficient to allow differentiation from the source rock itself, which is known to contain paramagnetic clays and small, single-domain or multi-domain ferrimagnetic particles in the rock.\textsuperscript{18-20} The present study is aimed at determining the relative concentration (and hence quantity) of nMag that would be needed to detect its presence. We have previously developed
methods to characterize minerals and rock formations using low field magnetic susceptibility\textsuperscript{19-22} and so, in the present study, we have used this technique to determine the relative signal from nMag in the presence of typical proppant materials and compared it to real shale gas core samples.

**Results and Discussion**

A typical magnetite nanoparticle (nMag) synthesis was chosen for the present studies involving the thermal decomposition of iron(III) acetylacetonate [Fe(acac)\(_3\)] in the presence of a suitable capping agent.\textsuperscript{23,24} While we have shown that the identity of the surface functionalization is important in controlling the mobility of a nanoparticle through a reservoir or proppant pack material,\textsuperscript{9} in the present case an oleic acid functionality was chosen so that solutions in hexane could be prepared.

![Size distribution obtained via small angle X-ray scattering (SAXS) of the magnetite nanoparticles in hexane (9.5 g/L).](image)

**Figure 2.1.** Size distribution obtained via small angle X-ray scattering (SAXS) of the magnetite nanoparticles in hexane (9.5 g/L).
The choice of hexane ensured that the solvent could be readily evaporated leaving the nMag dispersed upon the proppant material. Figure 2.1 shows the size distribution of the nMag to be within the range of 5-20 nm with an average of 11.8 nm, as determined by small angle X-ray scattering (SAXS). This is consistent with the transmission electron microscopy (TEM) image shown in Figure 2.2, which gives the particle size range of 6-23 nm and an average of 15 nm. Similar sized particles have been previously reported as MRI contrast agents.11-16

![Representative TEM image of the magnetite nanoparticles used in this study.](image)

**Figure 2.2.** Representative TEM image of the magnetite nanoparticles used in this study.

**Detectability of nMag versus proppant.** Two proppant materials were chosen for the study: sand and ceramic. To mimic a sand proppant pack we have employed frac sand (Unimin, 20-40 mesh), which is high purity quartz sand produced from sandstone with smooth round grains (Figure 2.3a) between 300-600 µm in size and a sphericity of 0.6.25 As a typical high strength ceramic we used CarboHSP (20-40 mesh, 400-840 µm) with a
supposed sphericity of 0.9, and a bulk density of 2.0 g/cm³ (Figure 2.3b). The composition of CarboHSP is Al₂O₃ (83%), SiO₂ (5%), TiO₂ (3.5%), Fe₂O₃ (7.0%), and other oxides (1.5%). The presence of iron oxide is expected to result in a significant magnetic susceptibility of the proppant, see below.

\[
\text{Figure 2.3. Scanning electron microscopy (SEM) images of (a) frac sand and (b) CarboHSP proppants.}
\]

Since the core magnetic susceptibility measurements were conducted using a handheld magnetic susceptibility meter (see Experimental Methods), it was appropriate
that the same instrument be used for the proppant pack. Prior to investigating the detection limit (signal-to-noise) for the nMag against each proppant, we prepared a sample of nMag infused sand and measured the magnetic susceptibility as a function of the depth under the surface of fresh sand (see Experimental Methods). The plot in Figure 2.4 shows that with the experimental set-up used the measured detection is limited to the surface (or within <1 mm of the surface).

![Magnetic Susceptibility vs Depth](image)

**Figure 2.4.** Plot of volume magnetic susceptibility of nMag (9.5 g/L)-infused Unimin sand as a function of depth under the surface of fresh Unimin sand. See Experimental Methods for details.

To determine how much nMag is needed in order to make a clear distinction between the two materials a series of spots of a known volume of standard solution of nMag was deposited onto a uniformly packed sample of frac sand (Figure 2.5a). Varying amounts of magnetite nanoparticles (100-500 µL) of a standard solution (9.5 g/L, $1.23 \times 10^{-4}$ mmol Fe), were added on top of a layer of uniformly packed sand (see Experimental Methods). The resulting array would mimic the presence of the nanoscale
contrast agent in the proppant pack at different concentrations. The magnetic susceptibility of the array was measured in 1.5 cm increments measurements in order to determine the spatial resolution of the instrument. Figure 2.5b shows the associated plot of volume magnetic susceptibility as a function of distance for the array in Figure 2.5a. Figure 2.5 shows the correlation between the position of the array and the magnetic susceptibility measurement. Figure 2.5b

![Figure 2.5](image)

**Figure 2.5.** (a) Photograph of an array of different volumes of a standard solution (1.23 x 10^{-4} mmol Fe, 9.5 g/L) of nMag adsorbed onto frac sand and (b) the associated plot of volume magnetic susceptibility as a function of distance (see Experimental Methods for details).

shows that as expected from its high quartz content, the frac sand has a net negative magnetic susceptibility, due to its diamagnetism.\(^{21,22}\) Furthermore, the usage of nMag with such proppant enables a clear distinction to be made between the two.

A similar set of measurements was made using a uniform pack of ceramic proppant. In this case the magnetic susceptibility measurements (Figure 2.6) shows that whilst there is a similar relationship of magnetic susceptibility with increasing
concentration of the nMag is observed, the proppant itself is slightly paramagnetic ($25.7 \times 10^{-5}$ SI), consistent with the presence of iron oxide as a constituent.

![Magnetic Susceptibility vs Distance](chart.png)

**Figure 2.6.** A plot of volume magnetic susceptibility as a function of distance for an array of different volumes of a standard solution ($1.23 \times 10^{-4}$ mmol Fe, 9.5 g/L) of nMag adsorbed onto CarboHSP (see Experimental Methods).

In order to ascertain the relative quantity of nMag required for differentiation against each of the proppants, samples were prepared by infiltrating a known amount of nMag solution into a known amount of proppant (see Experimental Methods). Using the magnetic susceptibility data in Table 2., it is possible to determine the concentration dependency of the magnetic susceptibility, as shown in Figure 2.7. These relationships can be used to determine the concentration of nMag that must be present to be able to differentiate nMag within the proppant pack.

The concentration required for the detection of nMag against a proppant pack can be estimated assuming that the magnetic susceptibility needs to have a value that can be differentiated from the proppant. For example, the magnetic susceptibility of sand is $-0.2 \times 10^{-5}$ SI and we can assume that a signal of $+0.2 \times 10^{-5}$ SI can be readily differentiated.
From Figure 2.7, we can calculate the concentration of nMag must be 0.269 g/L. In a similar manner, if it is assumed that in the case of CarboHSP a signal of 50% greater than

Table 2.1. Summary of experimental quantities for nMag/proppant samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass of Unimin sand (g)</th>
<th>Mass of CarboHSP (g)</th>
<th>[nMag] (g/L)</th>
<th>Magnetic Susceptibility (10^-5 SI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>10.01</td>
<td>-</td>
<td>-</td>
<td>-0.20</td>
</tr>
<tr>
<td>2.2</td>
<td>-</td>
<td>11.02</td>
<td>-</td>
<td>25.7</td>
</tr>
<tr>
<td>2.3</td>
<td>10.12</td>
<td>-</td>
<td>2.38</td>
<td>37.6</td>
</tr>
<tr>
<td>2.4</td>
<td>8.91</td>
<td>-</td>
<td>4.75</td>
<td>80.1</td>
</tr>
<tr>
<td>2.5</td>
<td>11.16</td>
<td>-</td>
<td>9.50</td>
<td>179.3</td>
</tr>
<tr>
<td>2.6</td>
<td></td>
<td>9.18</td>
<td>2.38</td>
<td>52.3</td>
</tr>
<tr>
<td>2.7</td>
<td>-</td>
<td>10.37</td>
<td>4.75</td>
<td>121.4</td>
</tr>
<tr>
<td>2.8</td>
<td>-</td>
<td>12.11</td>
<td>9.50</td>
<td>214.6</td>
</tr>
</tbody>
</table>

the background is needed then a concentration of nMag of 1.01 g/L is required. Given these numbers we can estimate the quantity of nMag as a function of the particle
concentration as compared to either the mass of proppant (sand or CarboHSP) or the volume of frac fluid used (Table 2.2).

Based upon the mass of proppant used (Table 2.1) we can estimate the amount of nMag required for each type of proppant (Table 2.2). Given that the cost of proppants vary between $0.22/kg (sand, $0.10/lb) and $1.32/kg (ceramic, $0.60/lb), and that we can estimate the raw material costs for nMag to be ca. $13,600/kg, the added cost ($0.9/kg sand or $3/kg ceramic) would be a significant increase over the proppant costs.

![Figure 2.7](image)

**Figure 2.7.** Plot of volume magnetic susceptibility of frac sand or CarboHSP proppant and nMag as a function of the concentration of nMag ($R^2 = 0.996$ and 0.986, respectively).

In a typical vertical well ca. 220,000 kg (100,000 lbs) of proppant are used. In contrast, a multi-stage frac job will use approximately 440,000-660,000 kg of proppant per stage, resulting in a total consumption as high as 5.4 million kg (12 million lbs). Thus, if we assume a value of 440,000 kg (200,000 lbs) for a single stage the amount of nMag required to allow detection above the background of the sand proppant is calculated from Figure 2.7 to be 29.6 kg (13.4 lb). In the case of a ceramic proppant such
as CarboHSP this value would be 101 kg (45.8 lb). With a multi-stage frac job a total amount of nMag could be as high as 4000 kg.

Table 2.2. Summary of estimated nMag required for detection above the proppant.

<table>
<thead>
<tr>
<th>Proppant</th>
<th>Conc. nMag for differentiation from proppant (g/L)(^a)</th>
<th>nMag required (kg/kg proppant)</th>
<th>nMag required for 2x10(^5) lb frac stage (kg)(^b)</th>
<th>nMag required for 3x10(^6) gal frac (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>0.269</td>
<td>6.72x10(^{-5})</td>
<td>29.6</td>
<td>1.48x10(^4)</td>
</tr>
<tr>
<td>CarboHSP</td>
<td>1.01</td>
<td>2.29x10(^{-4})</td>
<td>101</td>
<td>5.57x10(^4)</td>
</tr>
</tbody>
</table>

\(^a\) Values calculated from Figure 2.7. \(^b\) 1 lb = 0.454 kg.

The estimates above are based upon the relationship of the nMag to the proppant placed in the frac. However, this mass of proppant is placed using a large volume of water (frac fluid) and the proppant does not go to all the areas that are fractured. Thus, we need some estimation of the amount of nMag that would be required to maintain a concentration sufficient for detection based on the volume of water used in the frac fluid is also required. In Texas, estimates of water use for hydraulic fracturing vary from 10600 m\(^3\) (2.8 million gallons) to 21500 m\(^3\) (5.6 million gallons) per well.\(^27\) Taking a value of 3 million gallons and the concentration required, an estimate of the amount of nMag needed for a well based upon the frac fluid volume can be estimated, see Table 2.2.

Detectability of nMag versus shale gas reservoir rock. In the forgoing discussion we were simply concerned with the detection of nMag against a background of the proppant (Figure 2.8a) that creates a pack to maintain permeability of the well. However, the detection of nMag in the borehole will be against a background of not only the proppant, but also the oil/gas, connate fluids, and the reservoir rock itself (Figure
2.8b). We have previously shown that the petroleum reservoir fluids have a range of components for which the mass susceptibility may be measured; however, their contributions will be lower that that of the proppant or the source rock. In order to ascertain the levels of nMag required

![Figure 2.8](image)

**Figure 2.8.** Illustration of proppant in a fracture, with the highlighted areas showing (a) detection area against a background of the proppant versus (b) detection area against a background of proppant, oil/gas, connate fluids, and reservoir rocks.

Figure 2.9 shows the volume magnetic susceptibility of the core as a function of the reservoir depth. It is clearly seen that the reservoir rock is generally paramagnetic rather
than diamagnetic as a function of the mineral composition of typical shales. Paramagnetic clays like illite, \((\text{K},\text{H}_2\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,\text{(H}_2\text{O})]\), shows a small, positive magnetic susceptibility, while iron bearing paramagnetic minerals like siderite \((\text{FeCO}_3)\) have higher positive magnetic susceptibilities. A small concentration of a ferrimagnetic mineral would also give a significant positive magnetic susceptibility. For both shale cores there appears a representative background level of the magnetic susceptibility of \(ca\).
45x10^{-5} - 50x10^{-5} \text{ SI}. However, there are regions that have magnetic susceptibilities of >200x10^{-5} \text{ SI} (see Figure 2.9). These regions could be due to higher concentrations of ferrimagnetic particles or due to regions of a paramagnetic mineral like siderite.

Using the quantitative data discussed above, we can calculate the quantity of nMag required to differentiate from a representative background and the peak values (Figure 2.9). The results are given in Table 2.3. A comparison of the concentrations required to be added to a frac fluid in order to differentiate the nMag from the reservoir rock are significantly higher than that needed to differentiate from the proppant. Between 8.64x10^4 and 2.43x10^5 \text{ kg per well} would be needed with a cost of $1-3 \text{ billion per well.}

**Table 2.3. Summary of estimated nMag required for detection above the reservoir rock.**

<table>
<thead>
<tr>
<th>Level of reservoir magnetic susceptibilitya</th>
<th>Conc. nMag for differentiation from reservoir rock (g/L)b</th>
<th>nMag required (kg/kg proppant) for 2x10^5 lb frac stage (kg)c</th>
<th>nMag required for 3x10^6 gal frac (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background</td>
<td>1.56</td>
<td>3.91x10^{-4}</td>
<td>172</td>
</tr>
<tr>
<td>Peak</td>
<td>13.2</td>
<td>3.29x10^{-3}</td>
<td>1450</td>
</tr>
</tbody>
</table>

a See Figure 2.9 for susceptibility values as compared to the reservoir rock. b Values calculated from Figure 2.7. c 1 lb = 0.454 kg.

**Concentration and removal of nanoparticles from water.** Occasionally there are claims in the media of hydraulically fractured wells leaking into the environment and contaminating ground water.\textsuperscript{28-30} These claims often involve the detection of chemicals that come from potential spills or leaks in the well.\textsuperscript{28,29,31,32} However, the concentration of the chemicals in the environment is low, due to the sheer volume of water, making it difficult to accurately determine the problem stems from the well or from natural sources.
While there are a few different types of tracers used for determining environmental contamination from hydraulically fractured wells,\textsuperscript{33-35} all of them require high concentrations of the material or chemical that is detected because of this. However, nMag could be easily adapted for use as an environmental contaminant tracer that would not require such large concentrations due to its magnetic properties.

\textbf{Figure 2.10.} Plot of the concentration of nMag before and after passing through column with a magnetic field applied. The starting concentration is 100 ppm. Solid bars represent the “before” concentration while empty bars represent the “after” concentration. There are error bars present on all data.

As nMag has a relatively high magnetic susceptibility, due to it being superparamagnetic, it could be used as an environmental contaminant tracer that can be concentrated down, or pulled from solution with a simple tabletop electromagnet. In order to determine the concentration at which nMag can be readily separated from the liquid it is suspended in, a tabletop electromagnet with a column was used as the source of magnetism and the nMag was passed through at a variety of concentrations (details can be found in Experimental Methods). As can be seen in Figure 2.10, at starting
concentrations around 100 ppm, significant amounts of nMag is held in the column with an applied magnetic field. There are a few data that either have the concentration of the solution after it passes through the column higher than the concentration of the solution before it passes through the column or the two data are similar. This could be due in part to the presence of steel wool used in the column; little pieces of the steel wool could have gotten into the solutions and given erroneous data. Regardless, this method works well for the majority of samples run, and so a smaller concentration was tried next.

**Figure 2.11.** Plot of the concentration of nMag before and after passing through column with a magnetic field applied. The starting concentration is 10 ppm. Solid bars represent the “before” concentration while empty bars represent the “after” concentration. There are error bars present on all data.

As can be seen in Figure 2.11, the majority of the nanoparticles pass through the column, despite the presence of a magnetic field when the concentration is 10 ppm, as opposed to 100 ppm. Much like what was seen in Figure 2.10, there are some data that
are significantly higher than 10 ppm for both starting and ending concentrations. This is most likely due to the presence of steel wool, which will add to the iron content if any small flakes get into solution. Thus, the minimum required concentration, out of the concentrations tested, is 100 ppm.

However, when calculated out, the required amount of nanoparticles would be 2,120 kg, or 2.12 tons. The cost of making this amount of nanoparticles will be in the tens of thousands of dollars, in addition to the cost of synthesizing the nMag used in tracing the fractures. However, it should be noted that the quantity required is less than the quantity required for detection, thus, if it is assumed that if the well were to leak or if there was to be a spill of the fracturing fluid, and the nanoparticles used as tracers were in the fluid, that concentration should be enough for separation with an electromagnet.

This is not a safe assumption. It is known that up to 70% of fracturing fluid can be lost during the fracturing process if protective measures are not in place.\textsuperscript{36,37} Thus, the concentration of the nanoparticles in a potentially contaminated environment would be significantly lower than the required 100 ppm for separation with an electromagnet. In order to resolve this problem, a different solution is required.

There have been reports of ceramic membranes being used as a means of waste water management,\textsuperscript{38} including at the industrial scale.\textsuperscript{39} This technology allows for the filtration of water at rates of approximately 18,000 to 21,000 barrels of water per day.\textsuperscript{39} The ceramic membrane used can filter out everything from hydrocarbons to bacteria and so it was adapted for use to concentrate water samples with nanoparticles suspended within (details in Experimental Methods). The membrane was able to concentrate the nanoparticles from 0.8 ppm to 20 ppm in 20 cycles. This means that in order to get an ending concentration of 100 ppm after 100 cycles, a typical number of cycles per day, the required starting concentration in the water would need to be $2.04 \times 10^{-8}$ ppm. If it is assumed that there is 5.6 million gallons of water being analyzed, this would mean there would only need to be 0.432 mg of nanoparticles in the water. This is significantly less
than required amount for detection which, when coupled with the fact this technology is already in use in the field, means that these superparamagnetic nanoparticles could be a cost-effective means of tracing contaminations from hydraulically fractured wells.

**Conclusions**

It is clear that while the quantities of the nMag are high as compared to biomedical applications, this work has demonstrated such materials could theoretically be used as contrast agents in shale gas reservoirs. The particles could be pumped into the well with the fracturing fluid and detected in the well via a volume magnetic susceptibility detector, similar to the one used in the above experiments. Additionally, it is worth noting that these nanoparticles could be easily adapted for use as a tracer in environmental contaminations through the use of existing technology. Unfortunately, the biggest issue would be the high cost of the quantities required. Two solutions to this are possible. First, the cost predictions used herein do not take into account either costs of manufacture of the nMag (which would increase the cost) or the lowering of costs through bulk manufacturing methods and alternative (cheaper) starting materials; only the cost of the starting materials used were calculated. Thus, significant lowering of costs would clearly be beneficial. Second, it would be useful for any downhole contrast agent to have an even higher magnetic susceptibility than nMag and particularly a higher magnetic susceptibility at downhole reservoir temperatures. It would be especially useful if the magnetic susceptibility were temperature independent across the range of temperatures experienced downhole. Thus, as the susceptibility of the reservoir rock and/or the proppant decreases with increasing temperature the signal-to-noise will be enhanced. In this regard, the superparamagnetic mixed oxide spinels, Mn\(_{(1-x)}\)Zn\(_x\)Fe\(_2\)O\(_4\), are known to have a higher magnetic susceptibility than magnetite making it an ideal candidate and worth further investigation.
Experimental Methods

**Materials.** Iron(III) acetylacetonate \([\text{Fe(acac)}_3\, 97\%]\), oleic acid \([\text{CH}_3\text{(CH}_2\text{-CH=CH(CH}_2\text{-CO}_2\text{H,\; 90}\%]\), oleylamine \([\text{CH}_3\text{(CH}_2\text{-CH=CH(CH}_2\text{)NH}_2,\; >70}\%]\), and 1,2-hexadecanediol \([\text{CH}_3\text{(CH}_2\text{)}_\text{13}\text{CH(OH)CH}_2\text{OH}]\) were obtained from Sigma Aldrich and were used without further purification. Citric acid monohydrate (Granular/Certified ACS, 99-102%) was obtained from Fischer Scientific. Benzyl ether (98%), hexanes (mixture of isomers), 1,2-dichlorobenzene (anhydrous, 99%), \(N,N'\)-dimethylformamide (anhydrous, 99.8%), ethyl ether (2000 µg/mL in methanol, analytical standard) and nitric acid (ACS Reagent, 70%) were obtained from Sigma Aldrich. Ethanol (200 proof) was obtained from Decon Laboratories Inc. NANOpure water™ was obtained through ThermoScientific. Sand was obtained from Unimin (Accupack, 20-40 mesh). CarboHSP (20-40 mesh) was obtained commercially. All materials were used as received.

**Characterization.** Size determination of the nanoparticles was achieved by small angle X-ray scattering (SAXS) using a Rigaku SmartLab X-Ray diffractometer using a Cu-K\(\alpha\) radiation source. Samples were prepared by sealing a concentrated nanoparticle solution in hexanes into a 1 mm “Glass Number 50 Capillary” tube (Hampton Research Inc.) and the data was resolved using Rigaku’s NANO-solver. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements were obtained on a Perkin Elmer Optima 4300DV. Samples were prepared by digesting 0.5 mL of concentrated nanoparticle solution in 9.5 mL of concentrated nitric acid. An aliquot of the digested solution (0.5 mL) was diluted into 9.5 mL of NANOpure™ water. ICP standards were obtained from Inorganic Adventures and diluted using NANOpure™ water. Images were obtained using a JEOL 2010 Transmission Electron Microscope (TEM) on Ultrathin Carbon Type-A support film (Ted Pella).
**Nanoparticle Synthesis.** The nanoscale magnetite was synthesized using a thermal decomposition reaction.\textsuperscript{23,24} To Fe(acac)\textsubscript{3} (706 mg, 2.00 mmol) in a 100 mL round bottom flask with a stir bar, was added oleic acid (0.951 mL, 1.50 mmol), oleylamine (0.987, 1.50 mmol), 1,2-hexadecanediol (0.388 g, 3.00 mmol), and benzyl ether (37.5 mL). The solution was heated to 200 °C under argon with constant stirring and held for 2 hours, before being heated to reflux and held for 1 hour. The solution was cooled to room temperature and then the nanoparticles were precipitated with ethanol (40 mL). The nanoparticles were centrifuged and washed with ethanol three times before air drying overnight, with a yield of 85%. The nanoparticles were then suspended in hexane (15 mL) in a 20 mL scintillation vial.

**Magnetic measurements.** Sand or CarboHSP was spread evenly into a 10.5” x 10.5” plastic tray, 0.5” deep. In the test, a 5 x 5 grid was prepared with 30 µL, 60 µL, 90 µL, 120 µL, and 150 µL of a nanoparticle solution (1.23x10^{-4} mmol Fe, 9.5 g/L) dropped into the five columns, respectively. Each row was a duplicate. The grid was covered with a layer of thin plastic wrap, so as to not contaminate the probe. The plastic wrap was first tested to see if there was any signal change; there was not.

Additionally, a beaker was filled with sand 1 cm deep. Nanoscale magnetite (30 µL) was added to the beaker and a measurement was taken. The probe was covered with a thin layer of plastic wrap. Then sand (0.1 cm) was added to the beaker and another measurement was taken, with the probe wrapped in a fresh layer of plastic wrap. Further 0.1 cm layers of sand were added and measurements undertaken until a diamagnetic signal (indicating just sand) was obtained.

Quantification versus the proppant was determined by placing nMag (2.50 mL, 9.50 g/L) into each of two 20 mL scintillation vials. Sand was added to one vial until only a small amount of nanoscale magnetite solution was not covered. The same procedure was repeated with CarboHSP. Additionally, an aliquot of nanoscale magnetite solution
was diluted to both half and quarter concentration and then added to two 20 mL scintillation vials (2.50 mL; 4.75 g/L, 2.38 g/L, respectively). Sand and CarboHSP were added to the vials in the same manner as before. The relative quantities for each sample are given in Table 2. All four vials were placed in a fume hood, uncapped, to let the hexanes evaporate. Once there was no visible liquid, the vials were gently heated to ensure dryness (40 °C). After cooling, the contents of each of the vials was mixed thoroughly and then placed into a quarter of a segregated plastic Petri dish and spread out evenly. In addition, a comparable quantity of sand and CarboHSP was put into quarters of a segregated plastic Petri dish. The low field volume magnetic susceptibility of the mixtures was then measured with a handheld probe magnetic susceptibility device (an MS2E Sensor, by Bartington Instruments). The probe was zeroed between each data point. Both the background (air) and the sample (sand, CarboHSP, and sand/nanoparticle or CarboHSP/nanoparticle solution) measurement were recorded. Sand and proppant measurements were taken between each solution spot. Solution measurements were taken in the middle of the solution spot. It should be noted that volume magnetic susceptibility is unitless. The use of SI indicates the International System of Units was used.

**Magnetic measurements on shale core samples.** Testing was conducted at Weatherford Laboratories (Houston, TX). Slabbed cores were supplied by Southwest Energy Company (Houston, TX). The two cores used in the experiments were the Harrison core, from Faulkner County, Arkansas and the Rackley core, from Cleburne County, Arkansas. The Harrison core had a total length of 359 feet (122 m), starting at a depth of 4240 feet (1445 m) and ending at 4599 feet (1567 m). The Rackley core had a total length of 713 feet (243 m), starting at a depth of 1970 feet (671 m) and ending at 2683 feet (914 m). Using the same handheld magnetic susceptibility probe as for the nanoparticles on sand experiment, measurements were taken by placing the handheld probe on the surface of the core at ambient temperature. On average, measurements were
obtained every four feet. Some measurements were taken closer together, a few mm apart, when a large volume magnetic susceptibility was detected. Other measurements were much further apart, due to missing sections of the core. A background reading, the shale core volume magnetic susceptibility, and the corresponding depth were recorded. The instrument was zeroed every 48 feet and the detector was wiped, so as to remove any accumulation of material from the core. Visual variations in the composition of the cores can be seen in Figure 2.10.

![Figure 2.12. Visual variations in the (a) Harrison and (b) Rackley cores can be observed, suggesting compositional differences.](image)

**Magnetic separation and concentration.** Magnetic separation was conducted with an S.G. Frantz canister separator with a column between the two coils that is tunable from 0-1.6 T. All magnetic separation tests were run at 0.3 T. The column was first rinsed with hexanes to remove any contaminants and then was packed with roughly 15 g steel wool after dry. Samples were then added to the columns at a rate of 0.2 mL/s. Aliquots were taken before and after being run through the column, as well as after the magnetic
field was turned off and the column rinsed with hexanes (15 mL). The column was rinsed and dried between each sample. Fresh steel wool was packed into the column after each sample. All samples were analyzed via ICP-OES.

In order to run the synthesized nMag through the ceramic membrane for concentration tests, it was first required to do a phase transfer to a hydrophilic surfactant. The synthesis followed was reported by Lattuada, et al. The as-synthesized nanoparticles (0.9684 g) were added to a 50/50 mixture of 1,2-dichlorobenzene and \( N,N' \)-dimethylformamide (73 mL and 49.77 mL, respectively). To this, citric acid was added (0.8072 g). The solution was stirred at 100 °C for 24 hours under an inert atmosphere. After heating, the solution was cooled to room temperature and then quenched with ethyl ether (40 mL). The nanoparticles were separated using a handheld magnet. The supernatant was discarded before the samples were washed with acetone several more times, with magnetic separation between each wash. The particles were allowed to dry overnight.

The water-soluble nanoparticles were then suspended in store-bought distilled water at 0.025 wt%, 0.0025 wt% and 0.00025 wt%. The filtration system used was a bench top model of a system developed by Molecular Filtration™ and AquapheX™. Three different filter sizes (0.14 \( \mu \)m, 300 kDa, and 8 kDa) were used to determine the best pore size. Each sample was collected (50 mL) and the rest was put into the concentration tank, which was then pumped through the ceramic filter. The solution that passes through the filter, permeate, was collected for later testing. The solution that does not make it through the filter, concentrate, is pumped back into the concentration tank to cycle through again. This was repeated until one tenth of the starting liquid remained. An aliquot was set aside for later testing. The filtration system, including the filters, was fully cleaned between each run.
References


Chapter 3

Mass susceptibility dependence on temperature and the composition of metal ferrites

Introduction

Each year there is an increasing demand for hydrocarbons.\textsuperscript{1,2} Although it has become easier to locate reservoirs, the hydrocarbons trapped therein are more difficult to obtain, as the oil and natural gas near the surface and in big, highly pressurized reservoirs have already been pumped out. This need for more oil and natural gas combined with the necessity of having to drill harder-to-obtain reservoirs, with the increase and improvement of technology, have begun to make previously economically unfeasible reservoirs big attractors for power generation. In the United States, the largest potential energy source is found in shale.\textsuperscript{3-6} It is, however, difficult to obtain hydrocarbons from shale, as it is very porous but incredibly impermeable.\textsuperscript{7} It was only recently that it was economically viable to use a technique called hydraulic fracturing to be able to successfully obtain hydrocarbon from shale.\textsuperscript{8} In order to obtain the maximum amount of production from a well, information is needed from the well itself during this hydraulic fracturing process.\textsuperscript{9} One of the ways to do this is to use a tracer in order to determine how well formed the fractures are.

As has been reported,\textsuperscript{10} the use of non-toxic nanoscale magnetite could be a viable tracer, as it has magnetic properties that could be taken advantage of and modified to be observed against background rock. However, previous studies have only measured the magnetic properties of magnetite, or other spinel ferrites, at room temperature or below.\textsuperscript{11-23} Shale rock reservoirs are often significantly hotter, usually 120-150 °C, as the further into the Earth is drilled, the hotter the well becomes.\textsuperscript{24,25} Magnetic properties are well known to decrease as temperatures increase, which means that although the magnetic properties of magnetite may be strong at room temperature, the magnetic
properties have a potential to significantly decrease as temperature increases.\(^{26}\) This decrease in magnetic properties, specifically mass susceptibility and mass magnetization would decrease the signal-to-noise ratio of the nanoparticles against the background rock.

In this study the dependence on temperature of mass susceptibility and mass magnetization of various manganese and zinc ferrites were studied. The dependence of mass susceptibility and mass magnetization on composition was also studied in order to determine if a means of prediction could be used to determine how the magnetic properties of the nanoparticles would change down well.

**Results**

**Mass susceptibility as a function of Mn:Zn ratio.** One of the goals of this study was to determine if particles of different compositions could be easily distinguished from each other through measurement of the temperature dependence of their mass susceptibility (\(\chi_{\text{mass}}\)). Figure 3.1 shows the plot of the mass susceptibility (\(\chi_{\text{mass}}\)) as a function of the ratio of manganese to zinc changes at a low magnetic field (17.5 mT). Nanoscale magnetite (i.e., no manganese or zinc) has a low, positive mass susceptibility (Figure 3.1, squares), whereas the other compositions studied had higher magnetic susceptibilities at the temperatures studied (27 °C and 125 °C). Starting from the left side of Figure 3.1, as the quantity of zinc decreases and the quantity of manganese increases, the mass susceptibility increases dramatically. However, above a ratio of 0.4, further increase in the amount of manganese results in the mass susceptibility decreasing slightly. Based on these results, the maximum susceptibility is obtained with a Mn:Zn of approximately 0.4. Although the mass susceptibility of each composition is different, some of the compositions have mass susceptibilities that are similar at both 27 °C and 125 °C, making it difficult to easily distinguish them. For instance, the mass susceptibility of Mn:Zn ratio of 1.89 has a very similar mass susceptibility at 27 °C when compared to the mass susceptibility of Mn:Zn ratio of 4.67 (114,000 \(10^{-8}\) m\(^3\)/kg and
108,000 $10^{-8}$ m$^3$/kg, respectively). Depending on the sensitivity of the detector and any errors, it might be impossible to distinguish the composition ratio Mn:Zn 1.89 from the ratio Mn:Zn 4.67.

**Figure 3.1.** A plot of mass susceptibility ($\chi_{\text{mass}}$) as a function of Mn:Zn ratio for MnZn ferrite nanoparticles. The filled shapes correspond to 27 °C. The open shapes correspond to 125 °C. The squares correspond to nanoscale magnetite.

Regardless of the similarities in signal between different compositions, each signal for MnZn ferrite nanoparticles is at least three times larger than the signal obtained from nanoscale magnetite (Figure 3.1, squares). There was a study done earlier that reported the quantity of nanoscale magnetite required for detection if the background and the proppant of choice was taken into consideration.\(^{27}\) When the same calculations are run for the composition with the highest signal, $6.29 \times 10^{-8}$ g and $2.20 \times 10^{-5}$ g would be needed to obtain a signal at least 50% greater than a background of sand and CarboHSP, respectively. If the assumption is made that there would be one million pounds of sand or CarboHSP used in a fracking job, then 0.0028 kg and 0.88 kg of the composition with the
highest signal would be needed to give a signal that is at least 50% greater than the signal of sand and CarboHSP, respectively. This is significantly less than the quantity of nanoscale magnetite required for the same scenarios (29.6 kg and 101 kg, against sand and CarboHSP respectively). The paper also reports the quantity of nanoscale magnetite required for detection against the background of a shale core sample, but unfortunately in order to compare to the data presented herein, the mass of the core that was measured is required and is unavailable. Still, from the above calculations, it can be reasonably assumed that significantly less material would be required for detection than nanoscale magnetite.

The plot in Figure 3.1 also shows the influence temperature has on mass susceptibility. In all cases, mass susceptibility decreases as temperature increases, which is to be expected due to Curie law. Curie law is often written as seen in Eq. 3.1, where $\chi_v$ is magnetic susceptibility, $C$ is the Curie constant ($n\mu_0\mu^2_0/\kappa_B$), and $T$ is temperature in Kelvin.$^{24}$

$$\chi_v = C / T \quad (3.1)$$

As can be seen from Eq. 3.1, temperature is inversely proportionate to magnetic susceptibility so as temperature increases, magnetic susceptibility decreases. However, this is for magnetic susceptibility, not mass susceptibility. In order to convert magnetic susceptibility to mass susceptibility, Eq. 3.2 – 3.4 are required, where $M$ is the magnetization of the material, $H$ is the magnetic field strength, $\rho$ is the density of the material, and $\sigma$ is the induced magnetic moment per mass. From these equations, the magnetic susceptibility that is reported can be easily changed into mass susceptibility.

$$\chi_v = M / H \quad (3.2)$$
$$\chi_{mass} = \chi_v / \rho \quad (3.3)$$
$$\chi_{mass} = \sigma / H \quad (3.4)$$
When looking at the curves in Figure 3.1, however, there isn’t a clear correlation for this decrease across all of the compositions. Some obviously decrease more than others, but it is difficult to discern any pattern from the data. Additionally, there isn’t an obvious, significant pattern between mass susceptibility and composition or the decrease of mass susceptibility as temperature increases and composition, making it difficult to accurately predict how different compositions will affect mass susceptibility without further data interpretation.

Given the variation with temperature, it is worth looking to see how the temperature dependence of the susceptibility varies with Mn:Zn ratio. Figure 3.2 shows the change in mass susceptibility, $\Delta \chi_{\text{mass}} (\chi_{\text{mass}} 27 \, ^\circ\text{C} - \chi_{\text{mass}} 125 \, ^\circ\text{C})$, plotted as a function of Mn:Zn ratio in the nanoparticles. The trend that is observed is similar to that seen in Figure 3.1, with a peak appearing at Mn:Zn of approximately 0.4, meaning that even though nanoparticles that have more zinc in the crystal structure than manganese have the largest mass susceptibility, it also has the most temperature dependence and decreases the most as temperature increases. This trend, however, is not linear, thus making it more difficult to accurately predict the change in mass susceptibility as temperature increases. Additionally, it is still difficult to differentiate the two ratios whose changes in mass susceptibility are similar; the change in mass susceptibility for Mn:Zn ratio of 1.89 is very similar to the change in mass susceptibility for Mn:Zn ratio of 4.67 ($44,000 \times 10^{-8} \, \text{m}^3/\text{kg}$ and $34,000 \times 10^{-8} \, \text{m}^3/\text{kg}$, respectively). Although both showed a decrease in mass susceptibility, both the magnetic susceptibilities and the change in mass susceptibility as temperature increases are so similar that, depending on the sensitivity of the detector and any interference or errors that might occur, the signals would be indistinguishable.

**Mass magnetization as a function of Mn:Zn ratio.** A potentially better indication of how composition affects magnetic properties would be to look at the changes in mass magnetization ($M_{\text{mass}}$) as the quantities of manganese and zinc are varied
Figure 3.2. A plot of the change in mass susceptibility (χ_{mass} 27 °C – χ_{mass} 125 °C) as temperature increases as a function of Mn:Zn ratio in MnZn ferrite nanoparticles. Circles correspond to MnZn ferrite nanoparticles. The square corresponds to nanoscale magnetite.

Figure 3.3. A plot of mass magnetization (M_{mass}) as a function of Mn:Zn ratio of MnZn ferrite nanoparticles. The filled shapes correspond to 27 °C. The open shapes correspond to 125 °C. The squares correspond to nanoscale magnetite, whereas the circles correspond to MnZn ferrite nanoparticles.
in relation to each other. If just the mass magnetization is observed, at higher magnetic field (930 mT), with the exception of magnetite (Figure 3.3, squares), there is only very slight variation across compositional differences (Figure 3.3, circles). The change in mass magnetization, ΔM (M_{mass 27°C} − M_{mass 125 °C}), as temperature increases was analyzed, as seen in Figure 3.4, in order to see if any trend emerges. Again, magnetite stands out as having almost no change in the mass magnetization as temperature increases, whereas the change in the mass magnetization of MnZn ferrite nanoparticles have a slight downward trend, but it is not an appreciable decrease. This indicates that there isn’t much of a dependence of the decrease in mass magnetization as temperature increases on the compositional changes of MnZn ferrites.

**Figure 3.4.** A plot of the change in mass magnetization (M_{mass 27°C} − M_{mass 125 °C}) between two temperatures as a function of Mn:Zn ratio in MnZn ferrite nanoparticles. Circles correspond to MnZn ferrite nanoparticles. The triangle corresponds to nanoscale magnetite.
**Binary oxides.** In order to better understand the effect of manganese or zinc on both the mass susceptibility and mass magnetization, as well as the changes of the aforementioned as temperature increases, a series of Mn ferrite and Zn ferrite nanoparticles with different Fe:M ratios were synthesized and studied.

Tables 3.1 and 3.2 summarize the mass susceptibility and mass magnetization as temperature increases for Mn ferrite nanoparticles. There is a slight increase in both mass susceptibility and mass magnetization as iron concentration increases, but both properties stay relatively high, especially compared to magnetite (Figure 3.1, squares). Due to the lack of unique data points, it is difficult to see the temperature dependence of mass susceptibility or mass magnetization on the quantity of manganese, but from the data available it appears that having a greater quantity of manganese present in the nanoparticles results in a slightly lower mass susceptibility but also that there is less of a change in mass susceptibility as temperature increases.

**Table 3.1.** Summary of mass susceptibility and change in mass susceptibility for Mn ferrite nanoparticles.

<table>
<thead>
<tr>
<th>Fe:Mn ratio in the nanoparticle</th>
<th>$\chi_{\text{mass}}$ at 27 °C (10^{-8} m^3/kg)</th>
<th>$\chi_{\text{mass}}$ at 125 °C (10^{-8} m^3/kg)</th>
<th>$\Delta\chi_{\text{mass}}$ ($\chi_{\text{mass}}$ 27 °C − $\chi_{\text{mass}}$ 125 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.20</td>
<td>5.56x10^4 ± 2.6x10^3</td>
<td>3.46x10^4 ± 1.7x10^3</td>
<td>2.10x10^4</td>
</tr>
<tr>
<td>2.44</td>
<td>4.26x10^4 ± 2.9x10^3</td>
<td>2.42x10^4 ± 1.7x10^3</td>
<td>1.85x10^4</td>
</tr>
</tbody>
</table>

Additionally, the change in both mass susceptibility and mass magnetization are shown in Tables 3.1 and 3.2. The change in mass susceptibility for the Mn ferrite nanoparticles does not change dramatically as composition is altered. Although there is only a small amount of data in this study, when combined with the data obtained from the
MnZn ferrite nanoparticles, it can be postulated that changing the quantity of manganese in the nanoparticle does not affect the change in mass susceptibility in an appreciable amount. Thus, despite the complication in predicting mass susceptibility of Mn ferrite nanoparticles, the amount the mass susceptibility decreases as temperature increases will remain fairly constant and be predictable.

**Table 3.2.** Summary of mass magnetization and change in mass magnetization for Mn ferrite nanoparticles.

<table>
<thead>
<tr>
<th>Fe:Mn ratio in the nanoparticle</th>
<th>$M_{\text{mass at 27 °C}}$ (emu/g)</th>
<th>$M_{\text{mass at 125 °C}}$ (emu/g)</th>
<th>$\Delta M_{\text{mass}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.20</td>
<td>46.4 ± 0.091</td>
<td>38.5 ± 0.24</td>
<td>7.96</td>
</tr>
<tr>
<td>2.44</td>
<td>41.6 ± 0.024</td>
<td>33.0 ± 0.17</td>
<td>8.61</td>
</tr>
</tbody>
</table>

A slightly different trend emerges for the change of mass magnetization for Mn ferrite nanoparticles. Although increasing the quantity of manganese in the nanoparticle results in the decrease of mass magnetization, the same trend as is seen in mass susceptibility, the change in mass magnetization increases as the quantity of manganese in the nanoparticles is increased. Although there is only a small quantity of data for Mn ferrite nanoparticles, when combined with the trend observed for the change in mass magnetization for MnZn ferrite nanoparticles, it can be observed that as manganese quantity in the nanoparticles increases, there is an increase in the change of mass magnetization. Although a definitive trend cannot yet be determined, the prediction can still be made that as manganese content increases, there will be a larger decrease in mass magnetization as temperature increases, despite the mass magnetization not changing appreciably across a range of compositions.
Tables 3.3 and 3.4 list the mass susceptibility and mass magnetizations at different temperatures of Zn ferrite nanoparticles. The data clearly shows that as the amount of zinc in the nanoparticle increases, the mass susceptibility decreases rapidly. Although there is only a few points of data for the Zn ferrite nanoparticles, when combined with the data obtained from the MnZn ferrite nanoparticles, it can be readily postulated that as zinc content is increased in a nanoparticle, the mass susceptibility decreases sharply.

**Table 3.3.** Summary of mass susceptibility and change in mass susceptibility for Zn ferrite nanoparticles.

<table>
<thead>
<tr>
<th>Fe:Zn ratio in the nanoparticle</th>
<th>$\chi_{\text{mass}}$ at 27 °C (10$^{-8}$ m$^3$/kg)</th>
<th>$\chi_{\text{mass}}$ at 125 °C (10$^{-8}$ m$^3$/kg)</th>
<th>$\Delta\chi_{\text{mass}}$ ($\chi_{\text{mass}}$ 27 °C − $\chi_{\text{mass}}$ 125°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.03</td>
<td>1.58x10$^5$ ± 7.4x10$^3$</td>
<td>8.92x10$^4$ ± 4.910$^3$</td>
<td>6.90x10$^4$</td>
</tr>
<tr>
<td>2.47</td>
<td>7.53x10$^4$ ± 4.8x10$^3$</td>
<td>2.90x10$^4$ ± 1.9x10$^3$</td>
<td>4.63x10$^4$</td>
</tr>
<tr>
<td>1.88</td>
<td>2.79x10$^4$ ± 1.9x10$^3$</td>
<td>7.56x10$^3$ ± 5.3x10$^2$</td>
<td>2.03x10$^4$</td>
</tr>
</tbody>
</table>

**Table 3.4.** Summary of mass magnetization and change in mass magnetization for Zn ferrite nanoparticles.

<table>
<thead>
<tr>
<th>Fe:Zn ratio in the nanoparticle</th>
<th>$M_{\text{mass}}$ at 27 °C (10$^{-8}$ m$^3$/kg)</th>
<th>$M_{\text{mass}}$ at 125 °C (10$^{-8}$ m$^3$/kg)</th>
<th>$\Delta M_{\text{mass}}$ ($M_{\text{mass}}$ 27 °C − $M_{\text{mass}}$ 125°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.03</td>
<td>60.7 ± 6.8x10$^2$</td>
<td>45.7 ± 0.24</td>
<td>15.0</td>
</tr>
<tr>
<td>2.47</td>
<td>44.6 ± 7.6x10$^3$</td>
<td>30.7 ± 0.24</td>
<td>13.8</td>
</tr>
<tr>
<td>1.88</td>
<td>31.0 ± 7.5x10$^3$</td>
<td>17.6 ± 0.21</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Additionally, the change in mass susceptibility as temperature increases is quite drastic as the amount of zinc present in the nanoparticles is increased. It decreases rapidly
as the zinc content is increased, which, when combined with the data from MnZn ferrite nanoparticles, suggests that there might be a clear trend that could emerge. To further pursue this, the change in mass susceptibility was plotted as a function of Fe:Zn ratio in the nanoparticles (Figure 3.5). As can be seen, there is nearly a linear relationship between the change in mass susceptibility as temperature increases as a function of composition, meaning the amount the mass susceptibility will decrease as temperature increases can be predicted with a relative amount of ease.

![Figure 3.5](image.png)

**Figure 3.5.** A plot of the change in mass susceptibility ($\Delta \chi_{\text{mass}} = \chi_{\text{mass}} \text{ at } 27^\circ \text{C} - \chi_{\text{mass}} \text{ at } 125^\circ \text{C}$) as temperature increases as a function of Fe:Zn ratio in Zn ferrite nanoparticles.

When the mass magnetization of Zn ferrite nanoparticles is studied, a similar trend emerges to that seen with mass susceptibility. As the zinc content in nanoparticles is increased, there is a marked decrease in mass magnetization, which is nearly linear (Figure 3.6). This trend does not obviously match the trend seen with MnZn ferrite nanoparticles, but this discrepancy could be explained by the presence of manganese, as manganese was shown to not have much of an effect on mass magnetization. If there is
enough manganese present in the nanoparticle, there is a chance that it could negate the effect of the zinc present. This will be further explored in the next section.

The change in mass magnetization, however, is nearly unchanged across the various compositions of Zn ferrite nanoparticles that were synthesized. The change in mass magnetization is higher than that seen in Mn ferrite nanoparticles, which fits with the trend seen in the MnZn ferrite nanoparticles. Zinc appears to create a higher change in mass magnetization than manganese, but neither element seems to affect how the change in mass magnetization is affected by changes in composition. What this suggests is in addition to the ease of mass magnetization prediction via compositional changes, the change in mass magnetization as temperature is increased will be easily predictable as a function of composition.

![Figure 3.6](image)

**Figure 3.6.** A plot of the mass magnetization ($M_{\text{mass}}$) as a function of Fe:Zn ratio in the nanoparticle. The filled shapes correspond to 27 °C. The open shapes correspond to 125 °C.
For both Mn ferrite and Zn ferrite nanoparticles, each composition has a distinct mass susceptibility and mass magnetization. This ability to distinguish composition through the mass susceptibility and mass magnetization suggests the magnetic properties of the binary ferrite nanoparticles can be controlled via compositional differences during the synthesis. Additionally, these magnetic properties are more distinguishable for each of the compositions in the binary ferrite nanoparticles than the ternary ferrite nanoparticles. This suggests there is a better ability to control the substitution into the crystal lattice, and thus alter the magnetic properties, which makes sense, as there is only one metal to substitute into the crystal structure of magnetite as opposed to competing substitutions between two metals.

The causes of these trends seen for mass susceptibility, mass magnetization, and the change of both mass susceptibility and mass magnetization for ferrites are connected to the ion being placed into the lattice as well as the location of the substitutions and the spins on the ions in the spinel structure.\(^{28}\)

**Discussion**

When attempting to understand how the substitution of heterogeneous ions into a lattice changes the magnetic properties, it is often a good idea to understand the crystal structure first. As the Mn ferrite, Zn ferrite, and MnZn ferrite nanoparticles are, effectively, substituted nanoscale magnetite, the crystal structure of nanoscale magnetite must first be considered.

Both bulk magnetite and nanoscale magnetite have an inverse spinel structure.\(^ {29}\) Spinel structures are characterized by having A and B sites, where A sites are tetrahedral in coordination whereas B sites are octahedral (Figure 3.7). In a normal spinel structure, trivalent ions occupy all of the B sites while divalent ions occupy all of the A sites. In an inverse spinel, the trivalent ion occupies only A sites, while divalent ions occupy both A and B sites. It has been shown that, in magnetite, as size is reduced, the magnetic
properties change due to both restructuring of the A and B site occupancies as well as the existence of a surface spin disorder that interacts with the A and B sublattices.\textsuperscript{29,30} This dependence on sublattice structuring for the change in magnetic properties can be extended to other spinel structures.\textsuperscript{18,19,31-33} As different cations are substituted into the structure, their crystal field splitting energy (CFSE) gain will determine if the structure stays inverse spinel or if the Fe\textsuperscript{3+} cations will be redistributed into the octahedral sites and Fe\textsuperscript{2+} will be distributed into the tetrahedral sites, as well as to what extent this occurs. The CFSE gain is determined by the spins, or the number of unpaired electrons versus paired electrons as follows Hund’s rule, of the competing ions and which sub-lattice the ions will be occupying.

\textbf{Figure 3.7.} A spinel group structure. The gray tetrahedral with the green sphere in the middle shows the tetrahedral, A, sites. The blue octahedron with the blue sphere in the middle shows the octahedral, B, sites. The large gray spheres are the oxidizing ions, oxygen in the case of magnetite and ferrites. By David Schrupp. Dispersion at de.wikipedia [CC-BY-SA-2.0-de (http://creativecommons.org/licenses/by-sa/2.0/de/deed.en)], via Wikimedia Commons from Wikimedia Commons.
**Mn ferrite.** As manganese is added into the crystal structure of Mn ferrite nanoparticles, there are a number of properties that could affect the mass susceptibility or mass magnetization, which include the spin changes as iron is substituted out, the effect of the substitution on spin-spin coupling, and the size of the ion substituted in. Manganese ions are often found in two oxidation states, +2 and +3. In the synthesis described in the experimental section, a Mn$^{2+}$ ion is used, as was confirmed via X-ray photoelectron spectroscopy (XPS). In XPS, the Mn$^{2+}$ 2p peaks have a split of around 11.2 eV, as well as the appearance of a satellite feature around 647 eV, all of which is absent from Mn$^{3+}$ spectrum.$^{34}$ In order to confirm this, however, a close analysis of the Mn$^{2+}$ 3s peak is required; the split seen on this peak is about 6.0 eV for Mn$^{2+}$, whereas it is smaller for Mn$^{3+}$ and Mn$^{4+}$. As can be seen in Figure 3.8, the two 2p peaks are at 641.49 and 653.19 eV, with a split of 11.7 eV. Additionally, there is a satellite feature that appears at 645.4. Inset is the 3s peak, which shows a split of around 6 eV, confirming the starting material was not oxidized to Mn$^{3+}$.

![Figure 3.8. XPS of Mn 2p and inset of Mn 3s peaks from Mn(II) acetylacetonate.](image-url)
When XPS was run on various MnZn ferrite and Mn ferrite nanoparticles, the results were more ambiguous. There was not enough manganese in the sample to be able to get a good resolution of the 3s peaks in order to determine if the manganese was Mn$^{2+}$ or Mn$^{3+}$. When the Mn 2p peak is analyzed, there was a satellite feature, but it was very small and difficult to resolve, due to the lower quantity of manganese in the samples (Figure 3.9). Based on reports analyzing manganese ion oxidation states in Mn ferrites via various methods,\textsuperscript{35,36} it can be assumed that there are mostly Mn$^{2+}$ ions, with only a small quantity of Mn$^{3+}$ ions present. This means the ion is high spin in both octahedral and tetrahedral coordinations, as there are unpaired electrons in the orbitals. Due to this, the CFSE gain for manganese is 0 for both octahedral and tetrahedral sites.\textsuperscript{37} As the CFSE gain for Fe$^{2+}$ is larger than 0, this means that the Fe$^{2+}$ ions will prefer the octahedral sites and the Fe$^{3+}$ and Mn$^{2+}$ will occupy both the tetrahedral and octahedral sites, creating a partially inverted spinel.\textsuperscript{32,37,38} This mixed sub-lattice structure lends itself to the differences seen in the magnetic properties between magnetite and Mn ferrite, as the dominating A-B interactions are suppressed.\textsuperscript{32,38} This suppression lowers the ferrimagnetic properties and increases the superparamagnetic properties, which is what is observed. As the amount of manganese increases in the lattice, the mass susceptibility and mass magnetization increases. However, there are too few points to be able to make generalizations for higher quantities of manganese in the Mn ferrite nanoparticles. Additionally, the ionic radius for Mn$^{2+}$ in tetrahedral and octahedral coordination environments is 1.6 and 1.94 Å, respectively.\textsuperscript{39} Fe$^{2+}$ in an octahedral coordination is 1.84 Å. Fe$^{3+}$ in tetrahedral and octahedral coordinations are 1.26 and 1.58 Å, respectively. Mn$^{2+}$ is clearly larger than Fe$^{3+}$ in both tetrahedral and octahedral coordinations, whereas it is not significantly larger than Fe$^{2+}$ in an octahedral coordination resulting in a Jahn-Teller distortion of the lattice. This slight distortion breaks the octahedral symmetry of the B sites.\textsuperscript{32} This breaking of the symmetry gives rise to ferrimagnetic, and eventually superparamagnetic, properties as well as a higher dependence on temperature.\textsuperscript{40} Much
like the effect of spin on magnetization, there are not enough data points to be able to clearly make generalizations at larger quantities of Mn in Mn ferrite nanoparticles.

Diameter size of the synthesize Mn-ferrite nanoparticles obtained via small angle X-ray scattering (SAXS, Table 3.5) shows that there is not much of a change in size of the nanoparticles as manganese content is increased. This lack of diameter change, coupled with the diameter of magnetite (11.82 nm), suggests that the manganese was substituted into sites where iron is of a similar size. Even though manganese will substitute into both tetrahedral and octahedral sites, it prefers octahedral sites, as Fe$^{2+}$ and Mn$^{2+}$ are similar in size in B sites. As was stated above, this will cause the superparamagnetism to increase, which is what is observed.

![Figure 3.9](image-url)  
**Figure 3.9.** XPS spectrum of Mn 2p peak of Mn(II) acetylacetonate.

<table>
<thead>
<tr>
<th>Fe:Mn ratio in the nanoparticle</th>
<th>Nanoparticle diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.20</td>
<td>8.31</td>
</tr>
<tr>
<td>2.44</td>
<td>8.3</td>
</tr>
</tbody>
</table>
**Zn ferrite.** Zn ferrite has a very similar structure to Mn ferrite, but ends up with vastly different magnetic properties. This is often due to the fact that Zn$^{2+}$, the oxidation state found in the Zn ferrite lattice, is diamagnetic, compared to Mn and Fe being paramagnetic. The Zn$^{2+}$ ion has no unpaired electrons and has a CFSE gain of 0. Much like Mn ferrite, due to the CFSE gain of Zn being lower than that of Fe$^{2+}$, it creates a partially inverted spinel, as Fe$^{2+}$ will occupy the octahedral sites, but Fe$^{3+}$ and Zn$^{2+}$ will occupy both the tetrahedral and octahedral sites.\textsuperscript{33} What is interesting is note that bulk Zn ferrite only has BB interactions, due to the distribution of Zn into only the A sites and Fe into only the B sites, whereas nanoscale Zn ferrite redistributes both the Zn and Fe into both A and B sites, giving rise to the increase in AB interactions and thus an increase in magnetization and mass susceptibility over bulk.\textsuperscript{41-43} These AB interactions, however, tend to be ferrimagnetic, which means that as the Zn content increases in Zn ferrite nanoparticles, the mass susceptibility decreases, which is seen in Table 3.3. Additionally, the magnetic saturation point may not be fully reached, due to the ferrimagnetism.

The ionic size of zinc is also much closer in size to iron than manganese.\textsuperscript{39} In a tetrahedral site, zinc has an ionic size of 1.48 Å while in an octahedral site it is 1.76 Å. Fe$^{3+}$ is 1.26 Å in a 4 coordinate site and is 1.58 Å in a 6 coordinate site, while Fe$^{2+}$ is 1.54 Å in a 4 coordinate site 1.84 Å pm in a 6 coordinate site. As Zn is a bit smaller than Fe$^{2+}$ in both A and B sites and slightly bigger than Fe$^{3+}$ in both A and B sites, it creates some Jahn-Teller distortion of the lattice, in addition to the presence of spin-disordered surface layer, creating a canted spin that can increase magnetization.\textsuperscript{44}

As can be seen in Figure 3.10, the size of Zn ferrite nanoparticles is not as constant across a range of compositions, as compared to Mn ferrite nanoparticles. As zinc content in the nanoparticle increases, the size of the nanoparticle decreases, but is still around the same size as nanoscale magnetite (11.82 nm). A higher iron content with a small amount of zinc substituted in is much larger than the synthesized nanoscale magnetite. It has been
previously reported that increasing the quantity of Zn in a nanoparticle will decrease the size, which is contrary to what is observed.\(^{42}\) What this suggests is that there is a redistribution of zinc and iron into the A and B sites, causing the lattice parameter, and thus size of the nanoparticle, to change.\(^{45}\) As zinc, in tetrahedral and octahedral sites, is similar in size to Fe\(^{2+}\), but is larger than Fe\(^{3+}\), the redistribution of Zn\(^{2+}\) into more B sites than A sites, which is common in inverse spinel structures, will cause a lattice parameter increase. This redistribution, combined with the spin-distorted surface that stems from the oxygen vacancies and other surface effects, creates the change in the magnetic properties that is observed. The addition of zinc decreases the magnetic properties of the Zn-ferrite nanoparticles as well as the size, to an extent.

**Figure 3.10.** Size of nanoparticles as determined by SAXS as a function of Fe:Zn ratio in Zn ferrite nanoparticles.
**MnZn ferrite.** When MnZn ferrite is synthesized, there is competition between the substitution of Mn and Zn into the A and B sites of the spinel structure. At high quantities of manganese in MnZn ferrites, it has been shown that there is a decrease in superparamagnetism, due to a raising of the blocking temperature. As manganese content is decreased and zinc increased, the focus on what causes the change in magnetic properties shifts. Zinc has been shown to have a maximum saturation magnetization that then decreases as the zinc content increases which is similar to what is observed in Figure 3.1. Additionally, as zinc is smaller than manganese, there should be a slight decrease in size of the nanoparticle as zinc content increases. This decrease in size of the lattice causes spin canting and thus an increase in magnetization, to a point, whereas with larger particles, and a higher quantity of manganese, surface effects that stem from the substitution of cations on the surface of the nanoparticle become competitive.

![Figure 3.11. Size of nanoparticles as a function of Mn:Zn ratio in MnZn ferrite nanoparticles.](image-url)

As seen in Figure 3.11, with the nanoparticles synthesized, there is nearly no change in size, as Mn content increased, suggesting that the amount of Zn or Mn...
substituted into the nanoparticle isn’t substantial enough to distort the lattice too much, though the nanoparticles are smaller than magnetite (11.82 nm). This decrease in size compared to nanoscale magnetite suggests that even though there is only a small amount of Mn and Zn incorporated into the nanoparticle as compared to Fe, it is still enough to cause some amount of size decrease thus leading to the spin canting, larger surface effects from cation substitution, and superexchanges that increase the magnetic properties of the nanoparticles.

Conclusions

In conclusion, varying the composition of the nanoparticles has a direct effect on both the mass susceptibility and mass magnetization. Substituting different quantities of manganese and/or zinc into the crystal structure has the effect of raising the mass susceptibility and mass magnetization of the nanoparticles as compared to nanoscale magnetite.

As more manganese is incorporated into the nanoparticles, the mass susceptibility decreases slightly, but eventually levels off at high quantities of manganese. The change in mass susceptibility as temperature increases, however, remains fairly constant, thus presenting no real dependence on composition with regards to manganese. Mass magnetization, as compared to mass susceptibility, shows no appreciable change as composition is altered. As temperature is increased, the change in mass magnetization across the compositions also stays fairly constant.

Zinc, on the other hand, shows a high level of effect on mass susceptibility. As the zinc content in the nanoparticle is increased, the mass susceptibility decreases sharply. Additionally, the change in mass susceptibility as temperature increases shows a high dependence on zinc content; as zinc content increases, so does the change in mass susceptibility observed. This dependence is nearly linear, thus allowing for prediction of magnetic properties as composition is altered. Mass magnetization, much like mass
susceptibility, has a distinct decrease as zinc content in the nanoparticle is increased. However, much like the change in mass magnetization as temperature increases seen in Mn ferrite nanoparticles, there is nearly no dependence on composition for Zn ferrite nanoparticles.

When these two cations are combined in a single composition of MnZn ferrite nanoparticles, the properties that emerge, especially as composition is altered, are a merger of the independent dependencies observed in Mn ferrite and Zn ferrite nanoparticles. These dependencies on compositional changes, and lack thereof, are related to the oxidation state and thus the positioning of manganese in the lattice as well as the spin of the cation and surface effects caused by the incorporation.

**Experimental Methods**

**Materials.** Fe(acac)_3 [97%], Mn(acac)_2, and Zn(acac)_2·x(H_2O) hydrate, were obtained from Sigma Aldrich and used without further purification. Oleic acid [CH₃(CH₂)₇CH=CH(CH₂)₇CO₂H, 90%], oleylamine ([CH₃(CH₂)₇CH=CH(CH₂)₈NH₂, >70%], 1,2-hexadecanediol [CH₃(CH₂)₁₃CH(OH)CH₂OH, HDD], benzyl ether (98%), and hexanes (mixture of isomers) were all purchased from Aldrich and used as received. Ethanol (200 proof) from Decon Laboratories Inc. was used as received.

**Characterization.** Mass susceptibility and mass magnetization studies were performed on a Quantum Design MPMS SQUID System with a High Temperature furnace installed. The range of magnetic field used was from 9300 to 9300 Oe in 350.94 Oe increments. Samples were prepared by grinding a powdered form of the nanoparticles into a fine powder and weighing out tens of milligrams on a small piece of TaegaSeal PTFE Tape Commercial Grade, ½” wide. The tape was then carefully folded around the sample and rolled into a small oblong shape. Quartz wool was put into the copper sample holder followed by the sample and more quartz wool. This is to prevent the sample from
moving too much during measurements. Size determination of the nanoparticles was achieved by small angle X-ray scattering (SAXS) using a Rigaku SmartLab X-Ray diffractometer using a Cu-K\textsubscript{a} radiation source. Samples were prepared by sealing a concentrated nanoparticle solution in hexanes into a 1 mm “Glass Number 50 Capillary” tube (Hampton Research Inc.) and the data was resolved using Rigaku’s NANO-solver. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements were obtained on a Perkin Elmer Optima 4300DV. Samples were prepared by digesting 0.5 mL of concentrated nanoparticle solution in 9.5 mL of concentrated nitric acid. An aliquot of the digested solution (0.5 mL) was diluted into 9.5 mL of NANOpure™ water. ICP standards were obtained from Inorganic Adventures and diluted using NANOpure™ water. X-ray photoelectron spectroscopy (XPS) was conducted via PHI Quantera X-ray photoelectron spectrometer using an aluminum X-ray source at 1486.7 eV. Samples were prepared by first drying the sample and then placing it on a small piece of indium foil. Data was analyzed via MultiPak.

**Nanoparticle synthesis.** The synthesis used for the Mn ferrite, Zn ferrite, and MnZn ferrite nanoparticles is a thermal decomposition reaction.\textsuperscript{15,16} It is carried out in an oxygen-free three-necked round bottom flask. The overall ratio of metal (2 mmol) to surfactant was kept constant. In a general synthesis, 1,2-hexadecanediol (0.3876 g, 1.5 mmol), oleic acid (951.1 µL, 3 mmol), and oleylamine (987.1 µL, 3 mmol) in benzyl ether (37.5 mL, 197.28 mmol) was used for each run. When all chemicals were added argon was flushed through the system to remove any oxygen. The system was then heated to 200 °C at a rate of 10 °C/min. Once at 200 °C, heating was held constant for two hours. After two hours, heating was increased to reflux at the same rate of 10 °C/min. Once refluxing, heating was held constant for one hour. After one hour, heating was turned off and entire system was let cool to room temperature. Ethanol (40 mL) was added to the solution to precipitate out the nanoparticles. The solution was then split into
50 mL centrifuge tubes and centrifuged. The supernatant was discarded and ethanol (15 mL) was added to each tube to wash the nanoparticles. The samples were centrifuged and washed twice more, discarding the supernatant each time. After washing, the nanoparticles were allowed to air-dry overnight and then suspended in hexanes.

References


Chapter 4

Commercial scale synthesis comparisons for metal ferrite nanoparticles

Introduction

One of the major drawbacks to using nanoparticles in an industrial setting is the lack of commercial scale syntheses. The syntheses that do exist are often limited to a select few types of nanoparticles and only use a few different types of syntheses, despite the fact that the syntheses used may not be the best method to use to make nanoparticles with specific properties.\textsuperscript{1,2} It has been shown that different syntheses can lead to vastly different properties, even if the nanoparticles appear the same or very similar in terms of size and shape.\textsuperscript{1,3-5} There are a few reasons as to why there are only a few types of syntheses used in industry; cost of raw materials, quality control, product yield, safety of synthetic method, waste disposal, and environmental concerns are just a few factors to keep in mind when determining the efficacy of using a particular synthetic method.

In order to preserve the desired magnetic characteristics of MnZn ferrite nanoparticles, a synthesis that did not change the composition, size, or shape of the nanoparticles was desired. Additionally, it had to be cost-efficient to synthesize large quantities, meaning it needed a large yield, inexpensive starting materials, simple-to-maintain equipment, safe synthetic method, and disposable or recyclable waste. In this chapter, only a few of the above factors are tested, due to lack of available equipment.

Results and Discussion

As noted in the introduction, a key driving force for the development of the nanoparticles as tracers is the need to be able to produce the nanoparticles on an industrial scale. To that end, three scalable reactions were investigated and compared to see which one produces nanoparticles with the desired characteristics and with the highest level of control over size and shape, best size dispersion, lack of aggregation, and
compositional control with the least cost.\textsuperscript{6-8} In order to be able to determine the size and shape dispersion, as well as compositional accuracy, small angle X-ray scattering (SAXS), transmission electron microscopy (TEM), and inductively coupled plasma – optical emission spectroscopy (ICP-OES) were conducted.

**Synthetic comparisons.** The first reaction carried out was a thermal decomposition of an oleate complex.\textsuperscript{6} The first nanoparticles to be synthesized with this method were MnZn ferrite nanoparticles with a composition of 0.7:0.3 Mn:Zn. The cost of the starting materials is roughly $5.99 per gram, with a yield of around 95%. While this is not cheap, it is less than what it costs to synthesize the same nanoparticles through a thermal decomposition of metal acetylacetonates.\textsuperscript{9} Additionally, this was calculated using prices that were not bulk pricing and from the more expensive chemical supply companies, so it can be reasonably assumed that the price will decrease in some fashion, though it is difficult to say by how much.

![Figure 4.1](image.png)

**Figure 4.1.** The size and shape control of MnZn ferrite nanoparticles synthesized through a metal-oleate complex reaction as determined by a) SAXS and b) TEM (representative image shown). The scale bar (bottom left) is 50 nm.
In order to create nanoparticles of monodispersity and uniform composition throughout and between the nanoparticles, the oleate complex synthesized was a mixture of iron, manganese, and zinc as opposed to mixing each metal oleate complex separately. When the nanoparticles were analyzed in SAXS (Figure 4.1a), the average particle size was 11.2 nm ± 0.89, with TEM (Figure 4.1b) being in very close agreement (11.2 nm ± 1.26). As can be seen in Figure 4.1b, the nanoparticles are also highly spherical, which, as compared to the original synthesis used to make these nanoparticles, is promising for size and shape control.

The second synthesis was a modification of a synthesis utilizing sodium dodecylbenzenesulfonate (SDBS). This synthesis had significantly less control over the shape and size of the nanoparticles. The morphology seen in TEM shows an aggregated, non-symmetrical product with a large size distribution (Figure 4.2). Additionally, the nanoparticles would not suspend readily in any solvent, especially hexanes. In order to

![Figure 4.2](image.png)

**Figure 4.2.** A representative TEM image of the MnZn ferrite nanoparticles synthesized through the SDBS synthesis.
run SAXS, a concentrated sample is required. However, as the SDBS nanoparticles were not able to be suspended in high enough concentrations, they were unable to be analyzed via SAXS. As the synthesis had a very low yield, the price to synthesize these nanoparticle was not calculated, as it would be prohibitively expensive in order to make a large quantity.

The third and final reaction utilized triethylene glycol (TREG). This reaction proceeded so poorly that the nanoparticles synthesized were unable to be suspended in polar solvents as reported. In addition, several non-polar solvents were tried, but the nanoparticles did not suspend. Due to this, no analysis of the reaction was completed and the reaction was not further pursued. Much like the SDBS synthesis, the cost per gram of this synthesis was not calculated due to the inability to synthesize nanoparticles.

As two of the three chosen reactions produced nanoparticles capable of being analyzed, it was prudent to compare the two synthetic methods. As seen in Figures 4.1b and 4.2, the TEM images for both the oleate complex and SDBS reactions show distinct differences in the size, size distribution, and aggregation of the nanoparticles synthesized. If only TEM is consulted, the preferred synthesis to create large quantities of nanoparticles is the oleate complex synthesis. However, it is still unclear if the nanoparticles from either of the reactions were synthesized with the desired ratios of Mn:Zn as compared to the ratios found in the precursors.

Figure 4.3 shows the comparison of the two viable large scale syntheses through the comparison of the ratio of Mn(acac)$_2$:Zn(acac)$_2$ (precursors) against the ratio of Mn:Zn in the nanoparticle. The circle corresponds to the oleate complex synthesis whereas the triangle corresponds to the SDBS synthesis. As can be seen, the oleate complex synthesis highly correlates to the ideal compositional ratio (shown as a dashed line in Figure 4.3). The SDBS synthesis, on the other hand, poorly correlates. The high correlation also can be found in the ratio of Fe:(Mn+Zn) for both the precursors and the nanoparticles. For the oleate complex reaction, this ratio is 2.00 for the precursors and
3.03 for the nanoparticles. For the SDBS reaction, the ratio is much further off; it is 2.00 for the precursors and 0.794 for the nanoparticles.

Figure 4.3. Compositional comparisons between the oleate complex and SDBS syntheses, plotted as the ratio of Mn:Zn in the nanoparticle as a function of the ratio of Mn:Zn in the precursors. The oleate complex reaction is represented by the circle, while the SDBS reaction is represented by the triangle. The dashed line shows the ideal compositional ratio between precursors and nanoparticles.

Based on results from TEM, SAXS, and ICP-OES, it can be clearly seen that the oleate complex reaction was the ideal synthesis, with high levels of control over size and shape, size distribution, aggregation (or lack thereof), and composition. Thus, all further syntheses were conducted with the oleate complex reaction.

Scaling up the synthesis. During the comparison between different scalable reactions discussed above, the total amount of nanoparticles per synthesis was hundreds of milligrams to a few grams. In order to be able to use the nanoparticles as tracers in hydraulically fractured well as intended, significantly more material needs to be synthesized. In order to simplify scaling up the reaction, nanoscale magnetite (nMag) was synthesized, as it uses less precursors than MnZn ferrite nanoparticles, making it a
simpler reaction to run. In order to test the feasibility of scaling the synthesis, ten times more starting material was used. When analyzed via SAXS (Figure 4.4a), the average size of the nanoparticles was seen to be 24 nm ± 3. Analysis of the TEM images (Figure 4.4b) shows an average particle size of 27 nm ± 2, which is in close agreement, much like the agreement found in the smaller synthesis. It should be noted that the average size of nanoparticles from the scaled-up reaction is roughly twice that of the smaller synthesis. However, this is comparing nMag to MnZn ferrite nanoparticles. It is well known that the insertion of cations into the lattice of magnetite changes the size of the synthesized nanoparticles,\textsuperscript{11-15} thus making some of the size different observed here at least partially due to said substitution.

**Figure 4.4.** The size and shape control of nMag synthesize through a scaled-up metal-oleate complex reaction as determined by a) SAXS and b) TEM (representative image shown). The scale bar is 100 nm.

For a better comparison, a larger scale reaction was run for MnZn ferrite nanoparticles with 2.5 times the amount of starting materials as the smaller reaction,
**Figure 4.5.** The size and shape control of MnZn ferrite nanoparticles synthesized through a scaled-up metal-oleate complex reaction as determined by a) SAXS and b) TEM (representative image shown). The scale bar is 100 nm.

**Figure 4.6.** The plot of the ratio of Mn:Zn in the nanoparticle as a function of the ratio of Mn:Zn in the precursors. The dashed line shows the ideal compositional ratio between precursors and nanoparticles.
which gave a product that was roughly 2.5 times the amount of product of the smaller reaction.

The nanoparticles that resulted from this scaling were analyzed with SAXS, TEM and ICP-OES, as seen in Figures 4.5 and 4.6. Much like the results seen in both the smaller syntheses, the sizes obtained from SAXS and TEM are in close agreement (14 nm ± 1 and 16 nm ± 2, respectively) and the nanoparticles maintain the small size distribution seen earlier in addition to being of similar size to the nanoparticle synthesized by the smaller synthesis. ICP-OES indicated that the quantity of Mn:Zn found in the nanoparticles is the same as the Mn:Zn ratio of the precursors, meaning that even as the reaction is scaled to make larger quantities of nanoparticles, the ability of compositional control does not change. However, the larger scaled synthesis nanoparticles seen in Figure 4.5b are significantly different shape than those from the smaller synthesis; they are cubic as opposed to spherical despite having the same precursor ratio of Mn:Zn. This cubic structure could be due to impurities in the carboxylate precursor, length of time allowed to age during the growth stage, and/or an excess of fatty acid.$^{10,16-20}$

Due to the success of the scalable reaction, more Mn:Zn ratios of MnZn ferrite nanoparticles were attempted. When other compositions were synthesized, the nanoparticles failed to precipitate out of solution. The compositions that failed had high quantities of zinc as compared to manganese in the precursors. While Zn, Mn, and Fe are shown to complex readily with oleate,$^6,^5,^{21}$ in order to form mixed metal nanoparticles, the oleate complex must have a uniform distribution of the various metals throughout and those metal-oleate complexes must have similar decomposition temperatures.$^{10,18,22,23}$ At low concentrations of zinc, nanoparticles are readily synthesized and so it can be assumed that the oleate complex is equally mixed and uniform throughout. At higher quantities of zinc, however, nanoparticles do not form from the oleate complex, which suggests there
is some change in the mixture of the oleate complex, preventing the creation of mixed metal oxide nanoparticles.

In order to determine if the oleate complex was forming in a non-uniform manner with higher quantities of zinc, thermogravimetric analysis (TGA) was run on iron-oleate complex, manganese-oleate complex, zinc-oleate complex, and two different iron-manganese-zinc-oleate complexes of varying compositions.

Fe-oleate complex, Mn-oleate complex, and Zn-oleate complexes have TGA curves that are similar to that seen in literature (Figure 4.7a-c).\textsuperscript{5,6,10,21,24} The small increases in weight percent seen near the beginning of the TGA curve on all three oleate complexes is due to undried solvent that was still present in the sample. Iron has two distinct section of weight loss; the first section starts around 160 °C and goes until roughly 250 °C. The percentage of weight loss seen in the first section correlates to a single oleate ligand being dissociated from the complex. The second section of weight loss starts around 300 °C and the percentage of weight lost correlates to the remaining two oleate ligands dissociating. The middle section, where the rate of weight loss decreases, or where the slope of the graph flattens, is associated with the dissociation of oleate molecules that are weakly bound or are even free.\textsuperscript{10} Manganese-oleate has a similar curve when compared to iron-oleate, but with the temperatures associated with weight loss slightly higher, as well as slightly steeper rates of weight loss.

For manganese-oleate, the first section of weight loss occurs around 240 °C and the second around 400 °C. When compared to literature, however, TGA curves often only have one point of steep weight loss, as opposed to the two points seen in Figure 4.7b. This second point, much like that seen in iron-oleate (Figure 4.7a), could be due to the dissociation of weakly bound oleate molecules.

Zinc-oleate, however, has a very different TGA curve when compared to iron-oleate or manganese-oleate. There is only one point on the curve where weight loss is evident, although there are a few little bumps and changes in rate. The major weight loss
occurs between 150 °C and 500 °C. This weight loss correlates with the complete
dissociation of oleate molecules from the zinc.

**Figure 4.7.** TGA curves of a) Fe-oleate complex, b) Mn-oleate complex, and c) Zn-oleate complex.

An important piece of information to take away from Figure 4.7 is the change in rate of weight loss for each oleate occurs at a slightly different temperature. Each change in rate of weight loss is associated with different steps of nanoparticle synthesis.\(^6,10\) The slower rates of weight loss at lower temperatures are associated with the prenucleation stage, the slower rates after a high rate at slightly higher temperatures are associated with the nucleation stage, and the high rates at high temperatures are associated with the growth stage of the nanoparticles. The temperatures associated with this changes are key, as they indicate the temperatures needed in order to be able to trigger the appropriate stage. As different metal-oleates are mixed, these stages and temperatures need to be closely observed otherwise nanoparticle formation may not occur.
To that end, two different iron-manganese-zinc-oleate complexes were synthesized and analyzed via TGA and compared to the individual metal-oleate complexes discussed above (Figure 4.8). Figure 4.8a is the comparison of a Mn:Zn
mixture of 0.3:0.7. As can be seen, the curves for the various metal-oleate complexes do not line up nicely. The mixed metal-oleate complex has a prenucleation stage between 190 °C and 270 °C; iron- and zinc-oleate complexes have prenucleation stages that occur around the same temperatures, whereas manganese-oleate complex needs at least 240 °C in order to begin the prenucleation stage. The nucleation stage for the mixed metal-oleate complex begins at 270 °C but ends by 300 °C. Only iron-oleate complex completes the nucleation phase by that temperature. The formation of nanoparticles occurs at temperatures above 300 °C for the mixed metal-oleate complexes. While this is also true for the other metal-oleate complexes, if the oleate molecules have not dissociated fully, nanoparticle formation will be halted and the reaction will fail.

The second of the mixed metal-oleate complexes studied is quite different from the first. The curve for the various metal-oleate complexes more closely match the curve for the mixed metal-oleate complex (Figure 4.8b). The prenucleation stage occurs at temperatures lower than 270 °C, which is similar to that seen for the 0.3:0.7 Mn:Zn mixed metal-oleate complex. The nucleation stage still occurs at a relatively narrow temperature window, but there are two extra changes in weight loss rate seen that were absent in Figure 4.8a. The first of the bumps occurs around 365 °C and the second around 435 °C. The second bump is most likely due to a change in the rate of nanoparticle formation, as it is not very pronounced, but the first bump nicely lines up with the temperature required to begin nucleation in manganese-oleate complex. This allows for the eventual synthesis of nanoparticles at higher temperatures without the interference of poorly-dissociated oleate molecules. In order to guarantee the synthesis of nanoparticles, the different oleate complexes must be able to begin dissociation before nucleation or nanoparticle formation begins.

One potential way to remove this problem would be to create separate oleate complexes for each of the metals and then mix them during the thermal decomposition step. However, it has been shown that creating separate oleate complexes and then
mixing them later for thermal decomposition leads to a broader size distribution and a decrease in shape control. Another potential method is to use a different solvent with a higher boiling point to allow for the start of dissociation of all metal-oleate complexes present. Further development of scalable reactions needs to be conducted in order to facilitate the usage of MnZn ferrite nanoparticles as tracers.

**Conclusions**

A series of different scalable synthetic methods for the development of mixed metal ferrite nanoparticles was investigated. The hope was to find a simple, facile synthesis for the creation of commercial-sized quantities of nanoparticles with a range of compositions that could be easily adapted by industry. It was discovered, however, that reaction conditions are highly important when attempting a large-scale reaction. While size can be controlled easily, composition and shape control requires more precision.

In the most successful synthesis, the oleate complex reaction, there is a dependence on the precursor and intermediate mixture. In the reactions explored in this chapter, it was shown that a high presence of zinc-oleate in the mixture requires either a higher temperature all together or a longer decomposition time at a lower temperature before the temperature is increased at the nucleation stage of the reaction. Manganese-oleate, on the other hand, seems to have a similar thermal decomposition profile to iron-oleate and so does not require such level of control as zinc-oleate.

**Experimental Methods**

**Materials.** FeCl$_3$·6H$_2$O [97%], MnCl$_2$·4H$_2$O [99.9%], Zn(NO$_3$)$_2$·6H$_2$O [98%], Fe(acac)$_3$ [97%], Mn(acac)$_2$, Zn(acac)$_2$·xH$_2$O hydrate [powder], Fe(NO$_3$)$_3$·9H$_2$O [98%] were obtained from Sigma Aldrich and were used without further purification. Oleic acid [CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$CO$_2$H, 90%], 1-octadecene [CH$_3$(CH$_2$)$_{15}$CH=CH$_2$, 90%], sodium dodecylbenzenesulfonate [SDBS, technical grade], xylenes [≥ 98.5 +
ethylbenzene basis], hydrazine solution [35 wt. % in H2O], triethylene glycol [TREG, 99%], HPLC-grade H2O [CHROMASOLV® Plus for HPLC], and hexanes (mixture of isomers) were purchased from Sigma-Aldrich and used as received. Ethyl acetate was purchased from EMD Milipore and used as received. Sodium oleate was purchased from TCI Chemicals and was used as received. Ethanol (200 proof) was purchased from Decon Laboratories Inc. was used as received.

**Characterization.** Size determination of the nanoparticles was achieved by small angle X-ray scattering (SAXS) using a Rigaku SmartLab X-Ray diffractometer using a Cu-K$_a$ radiation source. Samples were prepared by sealing a concentrated nanoparticle solution in hexanes into a 1 mm “Glass Number 50 Capillary” tube (Hampton Research Inc.) and the data was resolved using Rigaku’s NANO-solver. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements were obtained on a Perkin Elmer Optima 4300DV. Samples were prepared by digesting 0.5 mL of concentrated nanoparticle solution in 9.5 mL of concentrated nitric acid. An aliquot of the digested solution (0.5 mL) was diluted into 9.5 mL of NANOpure™ water. ICP standards were obtained from Inorganic Adventures and diluted using NANOpure™ water. Images were obtained using a JEOL 2010 Transmission Electron Microscope (TEM) on Ultrathin Carbon Type-A support film (Ted Pella). Thermogravimetric analysis (TGA) was conducted on a SDT Q600 under air atmosphere at 50 mL/min. Samples were placed in a puck (5-10 mg) and were heated to 600 °C at a rate of 5 °C/min.

**Nanoparticle synthesis.** Three unique, large-scale, thermal decomposition reactions were carried out in an inert atmosphere to synthesize both MnZn ferrite and nanoscale magnetite.$^{6-8}$

**Oleate complex reaction.** Ethanol, HLPC-grade H$_2$O, and hexanes were added to a mixture of metal salt(s) and sodium oleate. In the smaller scale reaction, metal salt(s) (4
mmol total) and sodium acetate (12 mmol) were mixed with ethanol (1.37 mol), HPLC-grade H$_2$O (3.33 mol), and hexanes (1.06 mol). If MnZn ferrite nanoparticles were being synthesized, the combination of all of the metal salts had to add up to the total metal salt quantity specified. The solution was placed into a round bottom flask with a stir bar and thermometer and dissolved via stirring under argon with no heat. Once dissolved, the solution was heated to 70 °C and held for four hours. This creates the metal-oleate complex$^6$. After four hours, the solution was cooled to room temperature and washed three times with HPLC-grade H$_2$O in a separation funnel. The top, organic layer was collected into a pre-weighed crystallization dish and then the hexanes was evaporated. Once dry, the dish and product were weighed in order to calculate quantity of product. To the product, oleic acid and 1-octadecene were added (smaller scale reaction used 2 mmol oleic acid and 0.079 mol 1-octadecene). The product was dissolved then transferred into a second round bottom flask. The solution was heated to reflux under an atmosphere of argon and held at reflux for 30 minutes. After, the solution was cooled to room temperature and then precipitated with ethanol (50 mL). The solution was centrifuged and washed twice more before allowed to air dry. The nanoparticles were then suspended in hexanes.

SDBS reaction. A solution of SDBS (10 mmol) and xylenes (30 mL) was sonicated in a bath sonicator for a minute. Meanwhile, FeCl$_2$·4H$_2$O (1 mmol), Fe(NO$_3$)$_2$·9H$_2$O (2 mmol), MnCl$_2$·4H$_2$O (1.05 mmol), and Zn(NO$_3$)$_2$·6H$_2$O (0.45 mmol) were added to ethanol (1.5 mL) before being added to the SDBS solution in a round bottom flask under vigorous stirring. The resulting solution was stirred for twelve hours at room temperature and under normal atmosphere. At the end of twelve hours, the solution was put under an argon atmosphere and heated to 90 °C. Once heated, hydrazine solution (5 mmol) was added. The solution was then refluxed for five hours. Once refluxing was complete, the solution was cooled to room temperature and precipitated
with ethanol. The solution was then centrifuged and washed several times before being air dried. Once dry, the nanoparticles were suspended in hexanes.

*TREG reaction.* A mixture of metal acetylacetonate (2 mmol) was put into a round bottom flask and triethylene glycol (25 mL) was added. A ratio of 0.7:0.3 Mn:Zn was used, with there being twice as much iron as manganese and zinc combined. The solution was put under an argon atmosphere and slowly heated to 180 °C and then held for 30 minutes. The solution was then heated to reflux and held for 30 minutes before being cooled to room temperature. Ethanol (10 mL) and ethyl acetate (20 mL) were added. A handheld magnet was then used to separate the nanoparticles from solution. The nanoparticles were washed three more times with a combination of ethanol and ethyl acetate before being air dried. Once dried, the nanoparticles were suspended in a polar solvent.

**References**

Chapter 5

Conclusions

The main focus on this work was on synthesizing and characterizing mixed metal ferrites to be used as tracers in hydraulic fracturing. I demonstrated the means by which such tracers could be synthesized, both in the laboratory and industrial settings, as well as the dependence of mass magnetic susceptibility on temperature and composition. Additionally, I have demonstrated the feasibility of using mixed metal ferrites as tracers, both in the fractures down well and in the environment, as a means of determining sources of contamination and leaks.

It was shown that although the synthesis used for creating mixed metal ferrite nanoparticle is easily adaptable to synthesizing a wide range of metal ferrite nanoparticles, the ability to create monodisperse nanoparticles with a controllable composition relies on a range of variables as the metals are changed. For some metals, there is a high level of compositional control, while for others, the predictability is not a direct correlation of the ratio of reagents to the ratio of metals in the nanoparticles. In such metals (e.g., aluminum), there is a heavily dependence on the kinetics of decomposition of reagents. Aluminum acetylacetonate is known to have a high thermal stability and thus less aluminum was incorporated into the nanoparticles. Additionally, this stability has been shown to create larger sized nanoparticles due to the decreased seed formation rate and higher growth rate, which is typically seen in reaction conditions with reduced precursor concentrations. I demonstrated that in order to circumvent this problem, a different precursor with a lower thermal stability and higher ligand exchange rate would be required.

It was also shown compositional control for some metals (e.g., gadolinium) can depend on various reaction conditions, such as heating rate, mixing rates, addition times of precursors, etc. In order to guarantee predictable compositional control, the reaction
must be well-monitored and controlled for all possible conditional variables, as well as matching kinetic decompositions of all precursors.

In order to such nanoparticles to be used as tracers in wells and in the environment, several requirements had to be met: cost of using the nanoparticles, detection against proppant, detection against shale gas reservoir rock, depth of nanoparticle detection, and ability and ease of removing the nanoparticles from the environment. It was shown that while the nanoparticles are not detected more than a millimeter under the surface of fresh sand with a small, handheld detector, relatively small quantities are required to be detectable against both proppsants and shale gas reservoir rock. If the proppant is diamagnetic, 0.269 g/L of nanoparticles would be required for detection. The quantity required for detection against non-diamagnetic proppant is, understandably, higher (1.01 g/L). Obviously, as shale gas reservoir rock has much higher magnetic susceptibilities than any of the proppants tested, a slightly higher concentration of nanoparticles are required for detection (1.56 – 13.2 g/L). Although this translates to a significant cost, that can be lowered through different synthetic routes or other such cost-cutting measures. Additionally, it was determined that the nanoparticles synthesized could be readily removed from the environment (water) through the use of a two-part methodology. The solution containing the nanoparticles would first be passed through a ceramic membrane already in use as a means of purifying produced and flowback water from a well for concentration of the nanoparticles to a detectable level and then passed through either a detector or an electromagnet for removal and analysis.

One of the drawbacks of the above testing, however, was the fact that it was conducted at room temperature. Shale wells are known to be much hotter than that, and thus the dependence of mass magnetic susceptibility on temperature was determined. I was able to show that there was a high level of dependence of mass magnetic susceptibility on composition of the nanoparticle. Although each particle had a decrease in mass magnetic susceptibility as temperature increased, each particle had a unique
“signal” that could be used as a means of “fingerprinting” a well or a source of contamination. It was determined that the dependence of mass magnetic susceptibility on composition was related to the quantity of incorporated metal and the location of said metal in the crystal structure of the nanoparticle. Therefore, by carefully controlling the composition of the nanoparticles, a wide range of unique “signals” could be synthesized and utilized in tracing. Additionally, I was able to show the dependence of mass magnetization on both temperature and composition, with similar results to mass magnetic susceptibility.

One of the biggest problems facing the use of nanotechnology in an industrial setting is the lack of material that can be synthesized at any given point in time. In order to be able to feasibly use the nanoparticles described above as tracers in the quantities required, I tested a few methods for commercial-scale synthesis. I determined that synthesizing such nanoparticles in large quantities requires modification of reaction conditions as composition is altered, due to the kinetics of the various precursors.

In order to fully utilize these nanoparticles on an industrial scale, there are some concerns and issues that need to be addressed. While the method I employed was capable of creating tens of grams of nanoparticles, actual usage of the nanoparticles in wells would require tens of kilograms, minimum. The current methods for synthesizing that large of a quantity of nanomaterial do not necessarily create particles with the best size, shape, or compositional control. I suggest that those synthetic methods be tested against the thermal decomposition method used in this work. Additionally, I suggest creating a single-step synthesis from the methodologies investigated herein, as they utilize oleates and solvents with high boiling temperatures. Merging the various methodologies into a single, continuous flow procedure will be difficult, but ultimately cost-effective, as it has the ability to create a method by which nanoparticles can be formed in an automated, controlled environment, while the solvents used can be recycled for later use.
The nanoparticles also need to be tested in the field on a large scale. I suggest obtaining samples of fracturing fluid from a collaborating company to first determine the mobility of the nanoparticles in the fluid as well as the interaction between the two and then the mobility of the nanoparticles as the fluid moves through the formation. This would allow for an understanding of how the surfactant used will cause interaction changes between the particle and the fracture, which will in turn demonstrate how well the nanoparticles could be used as tracers.

In conclusion, mixed metal ferrite nanoparticles were synthesized with a wide range of compositions, which, in turn, are able to be used as unique tracers due to the dependence of mass magnetic susceptibility on composition. This work demonstrates that although the cost of the nanoparticles is currently high, it is feasible to reduce it through the use of different synthetic methodologies. Additionally, it was demonstrated that the nanoparticles could be easily used as a tracer in the environment as a means of determining the source of contamination, or lack thereof.
Appendix A

Complete list of published articles


Appendix B

Reprint

DOI:10.1080/17458080.2013.832422.
Reagent control over the composition of mixed metal oxide nanoparticles

Alvin W. Orbaek\textsuperscript{a}, Lauren Morrow\textsuperscript{a}, Samuel J. Maguire-Boyle\textsuperscript{a} and Andrew R. Barron\textsuperscript{a,b,c,*}

\textsuperscript{a}Department of Chemistry, Rice University, Houston, TX 77005, USA; \textsuperscript{b}Department of Mechanical Engineering and Materials Science, Rice University, Houston, TX 77005, USA; \textsuperscript{c}College of Engineering, Swansea University, Singleton Park, Swansea SA2 8PP, Wales, UK

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Binary (M\textsubscript{1}–M\textsubscript{2}–O) and ternary (M\textsubscript{1}–M\textsubscript{2}–M\textsubscript{3}–O) metal-oxide nanoparticles (NPs) have been prepared by thermal decomposition in benzyl ether of the appropriate M(acac\textsubscript{n}) (M = Fe, Mn, Pd, Cu, Al, Gd) compounds in the presence of a mixture of oleic acid and oleylamine templating (surface capping) ligands, and 1,2-hexadecanediol as an accelerating agent. The metal percentage and the particle size were investigated as a function of the starting composition. The NP composition is controlled by the relative reaction rates of the particular precursors, such that prediction of NP composition from reagent ratios is not straightforward. However, understanding reaction rate limitations allows for alternative synthesis to be developed. In some cases, ligand exchange reaction and subsequent decomposition are possibly more important than thermal decomposition.

Keywords: metal; oxide; nanoparticle; precursor; composition

1. Introduction

As a consequence of their potential applications as contrast agents, tracers, energetic materials and catalysts, there have been extensive research on the synthesis of nearly monodisperse metallic and metal oxide nanoparticles (NPs).[1] In the majority of applications, control over the size and size distribution are important considerations; however, where mixed metal oxides are desired then control over the atomic composition is also a factor. This is particularly true in the area of catalysis where small changes in composition can have large effects on the catalytic activity.[2–7] Recently, we have gained interest in the potential use of superparamagnetic NPs as traces in geological formations. The idea being that variation in the Curie temperature can be used as a method for differentiating one tracer from another and from naturally occurring background materials.

Common synthetic routes for the preparation of narrowly disperse metallic and metal oxide NPs include co-precipitation of metals salts, hydrolysis of metal salts (e.g. sol–gel), thermal decomposition of organometallic precursors, or the polylol process.[8–11] Among these methods, the thermal decomposition of organometallic precursors in non-coordinating, high-boiling organic solvents in the presence of templating/surface capping ligands has been proven to be a flexible method for polymetallic NPs with decent control over the size and distributions.[12]
The NP synthesis in non-coordinating solvents was originally developed for the synthesis of semiconductor nanocrystals,[13] based on the concept of providing reactive substituents to both components of the system,[14,15] however, recently it has become an attractive method for producing metallic and metal oxide NPs, e.g. via the one-pot synthesis of bimetallic oxide NPs by the thermal decomposition of metal acetylacetonate (acac) precursors in high temperature boiling ethers.[16,17]

We have previously reported that for the composition of cobalt–iron oxide (Co–Fe–O) NPs (i.e. Co:Fe ratio) as synthesised from the appropriate metal acac precursors, the Co concentration increases linearly with increasing Co(acac)₂ precursor concentration, and only a very small percentage of Co(acac)₂ was not directly incorporated into the NPs. [18] This suggested that the kinetics of the decomposition of each precursor [Fe(acac)₃ and Co(acac)₂] is near identical and that the composition of the NPs is statistically a function of the starting precursor mixture. In the course of our studies, we have become interested in whether compositional control can be extended to other systems and what factors of the precursor stability, structure and reactivity control the composition of the final NP. Our initial results in this area are described herein.

2. Experimental procedure

2.1. Materials

Fe(acac)₃ [97%], Fe(acac)₂ [99.95%], Cu(acac)₃, Al(acac)₃, Gd(acac)₃.2(H₂O) and Zn(acac)₂.x(H₂O) hydrate were obtained from Sigma Aldrich and used without further purification. Pd(acac)₂ and Mn(acac)₂ were obtained from Alfa Aeser and used as received. Oleic acid [CH₃(CH₂)₇CH=CH(CH₂)₇CO₂H, 90%], oleylamine ([CH₃(CH₂)₇CH(CH₂)₈NH₂, >70%], 1,2-hexadecanediol [CH₃(CH₂)₁₃CH(OH)CH₂OH, HDD], benzyl ether [98%] and hexanes (mixture of isomers) were all purchased from Aldrich and used as received. Ethanol (200 proof) from Decon Laboratories Inc. was used as received.

2.2. Characterisation

Size determination of the NPs was achieved by small angle X-ray scattering (SAXS) by a Rigaku SmartLab X-ray diffractometer using a Cu–Kα radiation source. Samples were prepared by sealing a concentrated NP solution in hexanes into a 1-mm ‘glass number 50 capillary’ tube (Hampton Research Inc.) and the data were resolved using Rigaku’s NANO-solver. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements were obtained on a Perkin Elmer Optima 4300 DV. Samples were prepared by digesting 0.5 mL of concentrated NP solution in 9.5 mL of concentrated HNO₃. A 0.5-mL aliquot of the digested solution was diluted into 9.5 mL of NANOpure™ water. The ICP standards were obtained from Inorganic Adventures and diluted using NANOpure™ water. The iron content was accumulated first for each set of particles, then the additional metal concentration was determined after, to avoid complications arising from emission wavelength overlap between the Fe and the additional metals. Scanning electron microscopy was carried out on an FEI Quanta 400 ESEM. Energy dispersive X-ray (EDX) analysis was performed using the energy dispersive detector in a FEI Quanta 400 scanning electron microscope. Samples were drop-coated onto a silicon wafer. The X-ray diffraction (XRD) was collected using a
Rigaku D/Max Ultima II diffractometer configured with a vertical theta/2-theta goniometer, Cu–Kα radiation, graphite monochromator and scintillation counter. Samples were prepared by precipitating the NPs out of solution, and drying before grinding the sample into a fine powder with a mortar and pestle. A zero-background sample holder was used. The sample was placed on the holder with some putty and a thin glass wafer and was pressed using a clean microscope slide to ensure the sample was level with the edge of the sample holder.

2.3. NP synthesis

Two similar methods were used for NP synthesis. Both were based on the methods previously reported.[12,17,18]

In the first general method, to a 100-mL three-necked round-bottomed flask was added the appropriate metal acac (0.75 mmol), HDD (0.3877 g, 1.5 mmol), oleic acid (0.951 mL, 3.0 mmol), oleylamine (0.987 mL, 3.0 mmol) and benzyl ether (37.5 mL, 193.5 mmol). The mixture was brought to reflux for 15 min, and then allowed to cool to room temperature. The particles in solution were precipitated with EtOH. The solution was then centrifuged for 5 min at 4400 rpm. The supernatant was discarded and the pellet made soluble in hexanes (ca. 10 mL) using light bath sonication to ensure complete solubility. This method was used for Fe–Pd–O and Fe–Al–O mixed metal oxide NPs.

An alternative synthesis was used for Fe–Al–O and Fe–Gd–O binary and Fe–Mn–Zn–O and Fe–Al–Gd–O ternary oxide NPs. The synthesis is carried out in an oxygen-free three-necked round bottom flask. The overall ratio of metal (2 mmol) to surfactant was kept constant. In the case of the Fe–Mn–Zn–O NPs, the amount of iron was kept constant, while manganese and zinc amounts were varied. In a general synthesis, HDD (2.5844 g, 10 mmol), oleic acid (1.902 mL, 6 mmol) and oleylamine (1.974 mL, 6 mmol) in benzyl ether (20 mL, 103.2 mmol) were used for each run. When all chemicals were added, argon was flushed through the system to remove any oxygen. The system was then heated to 200 °C at a rate of 10 °C/min. Once at 200 °C, heating was held constant for 2 hours. After 2 hours, heating was increased to reflux at the same rate of 10 °C/min. Once refluxing, heating was held constant for 1 hour. After 1 hour, heating was turned off and the entire system was let to cool to room temperature. Ethanol (40 mL) was added to the solution to precipitate out the NPs. The solution was then split into 50 mL centrifuge tubes and centrifuged. The supernatant was discarded and ethanol (15 mL) was added to each tube to wash the NPs. The samples were centrifuged and washed twice more, discarding the supernatant each time. After washing, the NPs were allowed to air-dry overnight and then suspended in hexanes.

A modified synthesis was used to make Fe–Al–O binary oxide NPs. The synthesis is carried out in an oxygen-free three-necked round bottom flask. The overall ratio of metal (2 mmol) to surfactant was kept constant. The ratio of iron to aluminium was varied in such a way that both metals combined equals 2 mmol. In the general synthesis, HDD (0.3877 g, 1.5 mmol), oleic acid (951.1 mL, 3 mmol) and oleylamine (987.1 mL, 3 mmol) in benzyl ether (37.5 mL, 197.28 mmol) were used for each run. When all chemicals were added, argon was flushed through the system to remove any oxygen. The system was then heated to 200 °C at a rate of 10 °C/min. Once at 200 °C, heating was held constant for 2 hours. After 2 hours, heating was increased to reflux at the same rate of 10 °C/min.
Once refluxing, heating was held constant for 1 hour. After 1 hour, heating was turned off and the entire system was let to cool to room temperature. Ethanol (40 mL) was added to the solution to precipitate out the NPs. The solution was then split into 50 mL centrifuge tubes and centrifuged. The supernatant was discarded and ethanol (15 mL) was added to each tube to wash the NPs. The samples were centrifuged and washed twice more, discarding the supernatant each time. After washing, the NPs were allowed to air-dry overnight and then suspended in hexanes.

3. Results and discussion

As noted in Section 1, we have previously reported that the composition of cobalt–iron oxide (Co–Fe–O) NPs (i.e. Fe:Co ratio) prepared by the thermal decomposition in benzyl ether of Fe(acac)$_3$ and Co(acac)$_2$, in the presence of a mixture of oleic acid and oleylamine surface capping ligands and HDD as an accelerating agent, is directly related to the composition of the metals in the precursor solution. However, the size and size distribution of the NPs were found to depend on the relative concentration of oleic acid, oleylamine, HDD and the metal precursor. To investigate the effect of reactant composition (M:M$'$), we have maintained the relative concentration of each reactant, including the total concentration of the metal precursors. Thus, the mixed metal oxide NPs (M–Fe–O and M–M$'$–Fe–O) have been prepared using the appropriate M(acac)$_n$ precursors. The elemental composition of the isolated NPs has been determined by ICP-AES (and EDX), while the particle sizes have been measured by SAXS and transmission electron microscopy (TEM) measurements.

The choice of the particular mixed metal compositions has been dictated by the desire to gain information on the uniformity of NP compositions for catalyst [6,7] and tracer applications. We have used Mn, Pd and Cu-doped Fe–O NPs as catalysts for the growth of single-walled carbon nanotubes (SWNTs). Since the composition of the catalyst can have a significant effect on the diameter and chirality of the SWNTs grown,[2–5] the more uniform a catalyst the more narrow the distribution of SWNT that will be grown. Our second application is for down-hole sensors for the oil and gas industry, in which the temperature-dependant low-field magnetic susceptibility is used as an identification tool. Small changes in composition will have a large change in the magnetic susceptibility. In this regard, the Fe–Mn–Zn–O and Fe–Al–Gd–O compositions are of interest.

3.1. Fe–Mn–O NPs

Figure 1 shows the composition of Fe–Mn–O NPs, as determined by the ICP-AES, prepared from various solutions of Fe(acac)$_3$ and Mn(acac)$_2$ (Table 1). Although the Mn concentration generally increases with increasing the Mn(acac)$_2$ precursor concentration (Figure 1, solid line) less Mn is incorporated into the NPs (see difference between solid and dashed lines in Figure 1). The composition was also determined for selected samples using EDX as a comparison to the ICP-AES analysis. These data are shown as the open squares in Figure 1. In general, the values are in agreement.

It should be recognised that ICP-AES analysis provides an average composition of the isolated NPs. At the extreme case, ICP-AES does not differentiate between samples of NPs that are solid solutions (i.e. Fe–Mn–O NPs) versus a mixture of NPs of different
compositions (i.e. Fe–O and Mn–O NPs). While it is also possible for composition to vary within individual particles,[19] we are interested in the uniformity over a small range of NPs. In this regard, a sample of the Fe–Mn–O NPs was spin coated onto a silicon wafer and the Fe and Mn contents were determined over different regions of the sample using EDX. Figure 2 shows the EDX analysis for samples 3, 4 and 9 of Fe–Mn–O; Figure 3 shows a representative example of the scanning electron microscopic (SEM) image associated with the EDX analysis. As may be seen from Figure 2(a) and 2(b) at low Mn content, there is a variation of composition across various areas analysed. In addition, the values are lower than the bulk analysis obtained by ICP-AES. At higher Mn content (Figure 2(c)), there is a wider range of values from EDX, but the average (40.2% Mn) is the same as that of the ICP-AES analysis (40.24% Mn). These results indicate that there is a range of Fe:Mn ratios between each Fe–Mn–O NP. While the ICP-AES analysis represents an average of the whole sample, individual particles can vary in composition as much as 30% (see Figure 2(c)).

The detailed mechanism of the synthesis of metal oxide NPs from M(acac)_n precursors at high temperature in organic solvents is not understood as clearly as the equivalent synthesis under hydrolytic conditions.[20] However, under the conditions used herein, there are two general mechanistic pathways that should be considered: (1) the direct thermal decomposition of the M(acac)_n precursor and (2) ligand exchange between the M(acac)_n and the HDD (Equation (1)) with the subsequent thermal decomposition of the alkoxide compound. The role of the oleic acid or oleylamine appears to be that of capping agents on the surface of the growing NP; however, their role in the decomposition of the precursors cannot be discounted,

\[
M\text{(acac)}_n + \text{HO–R–OH} \rightarrow M\text{(acac)}_{n-1}(\text{O–R–OH}) + \text{acac–H}. \quad (1)
\]
Table 1. Summary of metal precursor composition for binary oxide NPs.

<table>
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<tr>
<th>Sample</th>
<th>Fe(acac)$_3$ (mmol)</th>
<th>Mn(acac)$_2$ (mmol)</th>
<th>Pd(acac)$_2$ (mmol)</th>
<th>Cu(acac)$_2$ (mmol)</th>
<th>Al(acac)$_3$ (mmol)</th>
<th>Al(OiPr)$_3$ (mmol)</th>
<th>Gd(acac)$_3$ (mmol)</th>
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(continued)
Figure 2. EDX analysis of various areas of samples 3 (a), 4 (b) and 9 (c) that were spin-coated onto silica. The value determined from ICP-AES is shown as dashed line.
In consideration of the first reaction pathway, the thermal decomposition temperature of Mn(acac)\textsubscript{2} (248°C) is significantly higher than that of Fe(acac)\textsubscript{3} (184°C) that would result in the incorporation of Fe in preference to Mn that is observed. With regard to the ligand exchange, it is difficult to find comparable data; however, a few general observations can be made. In the solid state, Mn(acac)\textsubscript{2} exists as the dehydrate, i.e. Mn(acac)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}, with Jahn–Teller distorted octahedral geometry as a consequence of its $d^5$ valence state.\[21\] It is expected that in the present reaction this geometry will be maintained in solution, albeit with solvent (benzyl ether) or an appropriate ligands (oleic acid or oleylamine or HDD) as axial ligands. Fe(acac)\textsubscript{3} also has a Jahn–Teller distorted octahedral geometry.\[22\] While the presence of three chelate ligands may be expected to stabilise the complex with regard to the ligand exchange, ligand exchange for Fe(acac)\textsubscript{3} is significantly faster than for other M(acac)\textsubscript{3} complexes.\[23\] Thus, the preferential incorporation of Fe over Mn is expected based upon the mechanisms understood to occur for M(acac)\textsubscript{n} formation of M–O NPs.

As shown in Figure 4, the Fe–Mn–O NP diameters and distributions, as measured by SAXS, are relatively constant (within particle size distribution) as a function of either the reaction composition or the composition of the isolated NPs. The SAXS data are in agreement with the TEM data (e.g. Figure 5), which give sizes for the NPs in samples 4 and 5 as 6 ± 2 nm and 7 ± 3 nm, respectively.
3.2. Fe–Pd–O NPs

The composition of Fe–Pd–O NPs prepared from solutions of Fe(acac)$_3$ and Pd(acac)$_2$ is shown in Figure 6. Although the Pd concentration generally increases with increasing Pd(acac)$_2$ precursor concentration, there is the same negative divergence from the reagent

Figure 4. Dependence of Fe–Mn–O NP size as a function of the metal precursor concentration.

Figure 5. TEM images of Fe–Mn–O NP prepared from Fe(acac)$_3$:Mn(acac)$_3$ ratio of (a) 60:40 (sample 4) and (b) 50:50 (sample 5), scale bar is 20 nm for each.
composition control that was observed in the Fe–Mn–O system. However, above 5% Pd, this appears to be minimalised. As a comparison to the analysis using ICP-AES, the Fe:Pd ratios were determined by EDX for samples drop-coated onto a silicon (see Section 2). As can be seen from Figure 6, the EDX analysis is slightly higher in each case and shows variation between the spot areas analysed. Again this suggests a slight inhomogeneity in the NPs.

The Fe–Pd–O NP diameters and distributions are relatively constant as a function of the reaction composition (Figure 7). The TEM images of selected Fe–Pd–O NPs (Figure 8) show no significant change in the size or shape with varying composition.

3.3. Cu–Fe–O NPs

Figure 9 shows the composition of Cu–Fe–O NPs prepared from solutions of Fe(acac)$_3$ and Cu(acac)$_2$. The Cu concentration increases with increasing Cu(acac)$_2$ precursor concentration (solid line) and follows the ideal relationship (dashed line) closer than that observed for the Fe–Mn–O NPs. Below ca. 70% Cu, the behaviour is similar to that of the Fe–Mn–O system, i.e. iron incorporation is preferential over the copper. However, above 70% composition in the reagent solution, Cu is preferentially incorporated.

The particle size of the Cu–Fe–O NPs is generally larger with increased Cu content (Figure 10); however, it is interesting to note that above ca. 60% the size alters significantly. This mimics the compositional trend shown in Figure 9. The TEM images show that in addition to the changing size, the shape is a factor over 60% Cu. As seen in Figure 11(a), at high Fe content the typical NPs are faceted; however, at high Cu composition the morphology is that of aggregates (Figure 11(b)) similar to the single-crystalline
three-dimensional aggregates previously reported by Zhang et al. [24]. The size and size distribution as measured by the TEM for sample 19 (7 ± 3 nm) are within the range measured by SAXS (6.8 ± 2.5 nm).

The decomposition temperature of the Cu(acac)₂ is significantly higher (284 °C) than that of Fe(acac)₃ (184 °C), which would result in the incorporation of Fe in preference to Cu. This is observed at low Cu(acac)₂ concentrations, but less so that with Mn(acac)₂, which decomposes at a lower temperature than that of Cu(acac)₂ (Fe < Mn < Cu). This suggest that, in the case of the Cu–Fe–O NPs, ligand exchange reaction and subsequent decomposition are possibly more important than the thermal decomposition. The Cu(acac)₂ readily makes either mono or bis complexes with Lewis bases,[25,26] and as such it is expected that in the present reaction mixture the HDD or oleylamine (and possibly benzyl ether) would form complexes, and therefore, it is these coordination compounds that must be considered to be the ‘precursor’ to the formation of Cu–O fragments for NP growth. At high Cu content in the reaction mixture (samples 33, 34 and 35), a preference for Cu–O NP is observed. This would suggest that the growth around a Cu seed occurs preferentially with Cu rather than with the incorporation of Fe.

The XRD of samples 19 and 34 was collected. The sample 19 (Fe:Cu = 20:80) was too amorphous to get a diffraction and only the background was observed. By contrast, the XRD of sample 34 shows broad peaks assignable as (220), (311), (400), (422), (511) and (440) of magnetite (JCPDS file No. 19-0629), (see Figure 12(a)). From the Scherrer equation, the crystalline domain size in sample 34 is 94 Å: slightly larger than
for Fe–O NPs prepared by the same method (54 Å from Figure 12(b)). The larger crystalline domain size is in agreement with a larger particle size observed with increased Cu content (Figure 10). The fact that the magnetite peaks are not shifted suggests that phase separation occurs rather than a solid solution. This appears to be consistent with the TEM results.

3.4. Al–Fe–O NPs

The choice of a precursor with a very high thermal stability should force its incorporation into a NP to be as a function of ligand exchange, and thus allow for a comparison of the two processes. Al(acac)$_3$ is thermally stable (257 °C) and undergoes ligand exchange slowly compared to Fe(acac)$_3$.[23,27]

The attempted synthesis of Fe–Al–O NPs using Fe(acac)$_3$ and Al(acac)$_3$ showed less Al incorporated into the NPs than expected. In fact, at very low Al:Fe ratios the majority of samples had essentially no Al incorporated, while above an Al:Fe ratio of 0.5 the Al

Figure 8. Representative TEM image of Fe–Pd–O NP prepared using a Pd(acac)$_2$ concentration of 4% (sample 15).
Figure 9. Atomic percentage of copper incorporated into Cu–Fe–O NPs versus the amount Cu(acac)$_2$ used in the reaction. The ideal ratio is shown as dashed line.

Figure 10. Dependence of Cu–Fe–O NP size as a function of the metal precursor concentration.
Figure 11. TEM images of Cu–Fe–O NP formed from (a) Cu(acac)$_2$:Fe(acac)$_3$ = 20:80 and (b) Cu(acac)$_2$:Fe(acac)$_3$ = 80:20.

Figure 12. XRD of (a) Fe–Cu–O NPs (sample 34) and (b) Fe–O NPs prepared by the same synthetic method. The broad peak at 25° in (a) is due to the glass slide sample holder.
content reaches a maximum of 17%. Increasing the amount of Al(acac)$_3$ in the reaction mixture results in less Al being incorporated into the NPs (see Figure 13).

The size and size distribution of the Al–Fe–O NPs were determined by SAXS. As can be seen from Figure 14, the average size shows a general trend of increasing with decreased iron content in the reaction mixture. Given the low levels of aluminium incorporated in the final NPs, this is consistent with the prior results where a decreased metal precursor concentration results in larger NPs. Thus, it appears that the presence of the low reactive Al(acac)$_3$ behaves almost as a diluent in the formation of Fe–O NPs. Thus, at high Al(acac)$_3$ concentrations in the reaction mixture, the size of the NPs formed is similar to that of reducing the ‘active’ precursor concentration and hence the seed formation rate.

As expected with minimal Al incorporated into the NPs, the TEM images (Figure 15) show little change in the size or shape of the particles. Furthermore, the $d$-spacing from high resolution TEM images is within the experimental error of those expected for magnetite (Fe–O) NPs (8.39 Å).[28,29]

Given the high thermal stability and low rate of ligand exchange observed for Al(acac)$_3$ it is unsurprising that there is only minimal incorporation into the Al–Fe–O NPs. If ligand exchange (Equation (1)) is a valid pathway, and the product of such an exchange would be a metal alkoxide, then the use of an alkoxide precursor (with known ability to form the appropriate metal oxide) should enhance the incorporation of the metal into the NPs. In this regard, aluminium alkoxides are well known as precursors for alumina NPs.[20,30] We therefore investigated the synthesis of Al–Fe–O NPs using mixtures of Fe(acac)$_3$ and Al(OiPr)$_3$.

Figure 16 shows the composition of Al–Fe–O NPs prepared from solutions of Fe(acac)$_3$ and Al(OiPr)$_3$. The Al concentration increases with increasing Al(OiPr)$_3$ precursor concentration and follows the ideal relationship (dashed line) closer than that observed for the Fe–Mn–O NPs. Furthermore, unlike the reactions with Al(acac)$_3$ (see Figure 13) high
Al:Fe ratios can be achieved. The XRD of samples 45 and 48 was collected. Both show broad peaks assignable as (220), (311), (400), (422), (511) and (440) of magnetite (JCPDS file No. 19-0629). From the Scherrer equation, the crystalline domain size in sample 45 and sample 48 is 77 Å and 92 Å, respectively.

As noted above, the decomposition temperature and ligand exchange of Al(acac)₃ as compared to Fe(acac)₃ make it impossible to create Al–Fe–O NPs with high Al content, irrespective of the relative concentrations of the precursors in the reaction mixture. However, if an alternative Al precursor is employed that undergoes ligand exchange readily, the result appears to be more comparable kinetics of decomposition under the present conditions, i.e. \( k[\text{Fe(acac)}_3] \approx k[\text{Al(OiPr)}_3] \).

3.5. Fe–Gd–O NPs

In the examples studied above, although the uniformity in composition of individual NP may vary, the ICP-AES analysis of multiple samples prepared with the same reagent composition is within the experimental error (see Figures 6 and 9). Thus, the reproducibility of the reactions is high, allowing for predictability once the relationship between reagent composition and NP analysis is understood. During our studies, we determined that such reproducibility is not the case for the synthesis of Fe–Gd–O NPs.

Figure 17 shows the composition of Fe–Gd–O NPs prepared from solutions of Fe (acac)₃ and Gd(acac)₃. While the gadolinium concentration in the isolated NPs generally increases with increasing the Gd(acac)₃ precursor concentration and straddles the ideal relationship (Figure 17, dashed line), unlike the Co–Fe–O, Fe–Mn–O and Cu–Fe–O
systems there appears to be no clear trend to allow the prediction of the composition of the final NPs from the reaction mixture. The thermal decomposition temperature of the Gd \((\text{acac})_3\) (143 °C) is slightly lower than that of Fe(\text{acac})_3 (184 °C), which would be expected to result in the preferential incorporation of Gd over Fe, this is not observed for the binary (Fe–Gd–O) NPs, while it is observed for the ternary (Al–Fe–Gd–O) NPs (see below).

Initially, the poor correlation was assumed to be an issue with either the ICP-AES standards and/or the digestion process.\[31\] Consequently, several samples were re-analysed using the freshly prepared calibration solutions and with increased digestion times. Table 2 and Figure 17 show that irrespective of the ICP-AES protocol the compositional analysis remains within ca. 5%. However, repeating reactions multiple times gave different Gd:Fe ratios, e.g. 50% Gd (Figure 17 and Table 2). This suggests that while the analysis is accurate and representative, the composition depends on both the reagent ratio and other factors. To explore these variations we performed the reaction using the same precursor (and reagent) ratios but different reaction sequences.

Two batches of Fe–Gd–O NPs (sample 52) were prepared with different reaction protocols. In one version, the solvent was preheated to 200 °C, the metals, HDD, oleic acid and oleylamine were mixed separately and added. In a second route, the solvent and the

Figure 15. Typical TEM image of Al–Fe–O NPs with high resolution TEM image of an individual particle inset.
Figure 16. Atomic percentage of aluminium incorporated into Al–Fe–O NPs versus the amount Al(OiPr)$_3$ used in the reaction. The ideal ratio is shown as dashed line.

Figure 17. Atomic percentage of gadolinium incorporated into Fe–Gd–O NPs versus the amount Gd(acac)$_3$ used in the reaction. The ideal ratio is shown as dashed line. The use of open squares allows for repetitive analysis of the same sample.
metal complexes were preheated to 200 °C and then the oleic acid and oleylamine were subsequently added. In each of these cases, the Gd analysis was 5.30% and 5.90%, respectively, as compared to 15.03% when all the reagents are heated together. This suggests that for the Fe–Gd–O system the composition of the resulting NPs is very dependent on the small variations in the reaction conditions, e.g. rate of heating, mixing rates, etc.

The size and size distribution of the Fe–Gd–O NPs were determined by SAXS. As may be seen from Figure 18 the average size ranges from 5 to 7 nm for reactions mixtures with an Fe:Gd < 0.6. At higher Gd concentrations, the size shows a general trend of increasing with decreased iron content. A comparison of the size as a function of Gd in the reaction mixture or the isolated NPs shows that the particle size is controlled by the reaction composition rather than the product composition.

Table 2. Repetitive ICP-AES analysis of various Fe–Gd–O NPs showing analytical reproducibility.

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Figure 18. Dependence of Fe–Gd–O NP size as a function of the metal precursor concentration.
We note that Fe–Gd–O NPs have recently been shown to be effective for tumour therapy via magnetic field hyperthermia.[32] However, in this case the Gd composition was < 1%, and the synthesis was with the appropriate chlorides (FeCl₃, FeCl₂ and GdCl₃) in an aqueous sol–gel reaction.

3.6. Fe–Mn–Zn–O NPs

For ternary oxide mixtures, the issue of compositional control is further complicated. Mixed ferrites have been previously reported with using MnCl₂, ZnSO₄ and FeCl₃ as the precursors.[33] As with this prior work, the iron-precursor concentration was maintained constant, while the relative amounts of the Mn and Zn precursors [Mn(acac)₂ and Zn(acac)₂, respectively] were varied (see Table 3). As may be seen from the data in Figure 19, the composition of the resulting NPs, as measured by the Mn:Zn ratio, closely follows the ratio of the precursors, thus, allowing for the reproducible synthesis of NPs with desired composition. Furthermore, this suggests that the relative reaction rates of Mn(acac)₂ and Zn(acac)₂ are similar despite the differences in thermal stability (248 °C versus 135 °C–138 °C, respectively). Zn(acac)₂ is only a monomer in the vapour phase and is a trimer in the solid state, i.e. Zn₃(acac)₆, in which each Zn ion is coordinated by five oxygen atoms in a distorted trigonal bipyramid structure.[34,35] It is therefore interesting that despite the different thermal stability and differences in structure that would be expected to alter the relative reactivity, the incorporation of Mn and Zn is predictable.

The size and size distribution of the Fe–Mn–Zn–O NPs were determined by SAXS for all the compositions prepared. As may be seen from Figure 20, the average size ranges from 6 to 8 nm; however, the variation is within the size distribution. Thus, the size of the NP shows no significant dependence on the relative ratio of manganese and zinc. This is further supported by the TEM analysis of the NPs as shown in Figure 21.

Table 3. Summary of metal precursor composition for ternary oxide NPs.

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</table>
Figure 19. The ratio of Mn:Zn incorporated into Fe–Mn–Zn–O NPs as determined by ICP-AES versus the ratio of Mn(acac)$_2$:Zn(acac)$_2$ used in the reaction ($R^2 = 0.964$). Ideal ratio is shown as dashed line.

Figure 20. Dependence of Fe–Mn–Zn–O NP size as a function of the ratio of Mn(acac)$_2$:Zn(acac)$_2$ used in the reaction.
and size distribution of the NPs appear unaffected by the composition, their shape is less regular for those with higher Mn content. This result is distinct from the previous work by Arulmurugan et al. [33], which showed that the particle size decreased with the increased Zn content. The XRD of samples 62, 67, 69 and 71 shows magnetite phase across all the compositions (Figure 22). The crystalline domain sizes range from 59 Å (sample 62) to 123 Å (sample 67).

Figure 21. Examples of typical TEM images of Fe–Mn–Zn–O NP prepared using (a) Mn:Zn 0.9:0.1 and (b) Mn:Zn 0.2:0.8.

Figure 22. XRD of Fe–Mn–Zn–O NP (sample 62).
3.7. Fe–Al–Gd–O NPs

As the Mn and Zn precursors appear to be incorporated into NPs, at an equal rate, investigation of a ternary mixture where the metals appear to show highly different rates is instructive. As discussed above, aluminium shows low incorporation, while gadolinium is easily incorporated (albeit with a variability). Thus, the composition of Al–Fe–Gd–O NPs was investigated. Figure 23 shows the Al:Fe:Gd composition of both the precursor solution (Table 3) and the NP composition. The plot shows that in all cases the NP composition is higher in Gd and lower in Al than that expected from the reaction mixture. Furthermore, at low Fe(acac)₃ concentration the isolated NPs appear to be Gd₂O₃.

The size and size distribution of selected Al–Fe–Gd–O NPs were determined by SAXS. The size increased (from 7.57 to 11.157 nm) with decreasing Fe content; however, the distribution remained constant (± 1.63 nm).

4. Conclusions

We have investigated the ability to control the composition (and compositional uniformity) of mixed metal oxide NPs through the ratio of reagents in the reaction mixture. As seen from Table 4, there is compositional control for most of the NPs; however, the predictability is not necessarily a direct correlation (ratio of reagents = ratio in NP), instead once a calibration curve is obtained, a specific desired composition can be attained. It appears that where the kinetics of decomposition of the various metal precursors is similar then a direct correlation is obtained (e.g. Co–Fe–O, Cu–Fe–O and Fe–Mn–Zn–O); however, where the reactivity is slightly different, a deviation (albeit predictable) from the ideal is observed (e.g. Fe–Mn–O). However, when the reaction rate for one precursor is
vastly different from the other (e.g. Al(acac)₃ versus Fe(acac)₃), then alternative precursors (e.g. Al(OiPr)₃) must be used.

It is also important to note that since the particle size and shape may remain unchanged over a wide composition range, this cannot be used solely along with bulk analysis to ensure that the desired composition has been obtained across all the NPs in the sample, i.e. homogeneity is not guaranteed because the overall composition is that desired. As such researchers should be cautioned in assuming uniform composition.

Acknowledgements
Financial support of this work was from the Robert A. Welch Foundation (C-0002) and the Air Force Office Scientific Research (FA8650-05-D-5807).

References


Appendix C

Reprint

Detection of magnetic nanoparticles against proppant and shale reservoir rocks

Lauren Morrow\textsuperscript{a}, David K. Potter\textsuperscript{b} and Andrew R. Barron\textsuperscript{a,c,d}\textsuperscript{*}

\textsuperscript{a}Department of Chemistry, Rice University, Houston, TX 77005, USA; \textsuperscript{b}Department of Physics, University of Alberta, Edmonton, Alberta T6G 2E1, Canada; \textsuperscript{c}Department of Materials Science and Nanoengineering, Rice University, Houston, TX 77005, USA; \textsuperscript{d}Energy Safety Research Institute, College of Engineering, Swansea University, Singleton Park, Swansea SA2 8PP, Wales, UK

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With the expansion in the production of shale oil and gas, there is a desire to obtain detailed information of the downhole environment resulting from hydraulic fracturing (fracking). Nanomagnetite (nMag) has been proposed as a suitable contrast agent for magnetic imaging. In order to determine its suitability, 15 nm oleic acid-stabilised magnetite nanoparticles were synthesised and the magnetic susceptibility was measured and compared against two types of proppant. Although frac sand is diamagnetic (\(-0.20 \times 10^{-5}\) SI), ceramic proppant is paramagnetic (25.7 \(\times 10^{-5}\) SI) due to the presence of Fe\(_2\)O\(_3\). The quantity of the nanoparticles that would be required for differentiation against the background levels in the proppant pack was calculated to be 0.269 g/L for sand and 1.01 g/L for ceramic, which correlates to a minimum of 15,000 kg and 56,000 kg per well, respectively. In order to determine the contrast with the reservoir rock itself, the magnetic susceptibility was mapped for cores from two typical shale gas reservoirs (Harrison and Rackley, Arkansas), which show a general low level of paramagnetism (ca. 4.5 \(\times 10^{-5}\) SI). However, regions are observed with higher susceptibility (>200 \(\times 10^{-5}\) SI) necessitating the use of 242,000 kg nMag per well in order to provide contrast with the reservoir.

Keywords: magnetite; shale; nanoparticle; core; magnetic susceptibility

1. Introduction

Shale gas represents the largest fraction of natural gas in the continental United States. With an estimated 482 trillion cubic feet of hydrocarbon,[1] shale gas has the potential to be the primary energy source for power generation in the USA for the coming decades.[2–4] The ability to extract shale gas economically has been achieved by the use of horizontal drilling techniques and hydraulic fracturing. Hydraulic fracturing (also known as ‘fracing’ or ‘fracking’) uses water, proppant (sand or ceramic particles), and chemicals, pumped at high pressures into the well bore, to induce fracturing of the shale, creating permeability so the gas can migrate into the well bore and to the surface.

In order to maximise the recovery of oil and gas, it is important to obtain information on the extent of the fracture flow characteristics of the rock within the hydraulically fractured reservoir.[5] Characterisation has traditionally been accomplished using

\*Corresponding authors. Email: arb@rice.edu

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techniques such as seismic measurements and nuclear magnetic resonance well logging; however, these methods have limitations and new methods are being investigated, including: conductive polymers,[6] active or passive devices,[7] or proppant tracking materials.[8] The low porosity and permeability of many oil and gas reservoirs, even after hydraulic fracturing, means that any sensor or tracer material must have a size sufficiently small to allow for its transport through the fractured rock formation. Nanoparticles (NPs) offer potential because one can change the surface properties to allow mobility [9] and their core may have a range of properties that can be sensed or reported. As such, NPs represent a potential sensor/tracer material and a number of mechanisms have been suggested for detection.[10]

There has been significant research into the use of magnetite as a tracer in biological applications, such as in magnetic resonance imaging (MRI), taking advantage of the magnetic properties of the nanomagnetite (nMag) in order to create a large contrast between the particles and the surrounding tissue.[11–15] The non-toxic nature of nMag would also have an advantage on environmental grounds [16] and so it has been proposed that it should be possible to scale up this technology to the size of a reservoir using magnetic nanoparticles and a large magnetic source and receiver.[10] This approach has merit since it is already known that studying the magnetic anisotropy of the reservoir source rocks can give a good understanding of the characteristics and structure of such formations.[17]

Given that the function of the proppant is to hold open the cracks that are formed in the source rock (shale) during the frac process, the presence of a nanosensor would be most likely associated with the proppant pack. Thus, it is important to ascertain if nMag may be distinguished from typical proppant materials. The most common proppant is high quartz sand such as the hydraulic fracturing sand (frac sand) used herein; however, due to the low crush strength of sand, ceramic particles are often used as proppant and so we have also used a typical high density ceramic proppant (CarboHSP). In addition, since the resolution of the measurement will be lower than the size of the propped fractures (>300 nm depending on the size of the proppant particle), then in order to differentiate the nMag from the background rock, the concentration of nMag must be sufficient to allow differentiation from the source rock itself, which is known to contain paramagnetic clays and small, single-domain or multi-domain ferrimagnetic particles in the rock.[18–20] The present study is aimed at determining the relative concentration (and hence quantity) of nMag that would be needed to detect its presence. We have previously developed methods to characterise minerals and rock formations using low field magnetic susceptibility [19–22] and so, in the present study, we have used this technique to determine the relative signal from nMag in the presence of typical proppant materials and compared it to real shale gas core samples.

2. Experimental procedure

2.1. Materials

Chemicals used were iron (III) acetylacetonate (97%, Sigma Aldrich), oleic acid \([\text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}]\) (90%, Sigma Aldrich), oleylamine \([\text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_8\text{NH}_2]\) (>70%, Sigma Aldrich), 1,2-hexadecanediol [HDD, \(\text{CH}_3(\text{CH}_2)_13\text{CH(OH)}\text{CH}_2\text{OH}\)] (Sigma Aldrich), benzyl ether (98%, Sigma Aldrich), ethanol (200 proof, Decon
Laboratories Inc.), hexanes (mixture of isomers, Sigma Aldrich), nitric acid (ACS Reagent, 70%, Sigma Aldrich), and NANOpure water™ (ThermoScientific). Sand was obtained from Unimin (Accupack, 20–40 mesh). CarboHSP (20–40 mesh) was obtained commercially. All materials were used as received.

2.2. Characterisation

Size determination of the nanoparticles was achieved by small angle X-ray scattering (SAXS) using a Rigaku SmartLab X-Ray diffractometer using a Cu-Kα radiation source. Samples were prepared by sealing a concentrated nanoparticle solution in hexanes into a 1 mm ‘Glass Number 50 Capillary’ tube (Hampton Research Inc.) and the data was resolved using Rigaku’s NANO-Solver. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements were obtained on a Perkin Elmer Optima 4300 DV. Samples were prepared by digesting 0.5 mL of concentrated nanoparticle solution in 9.5 mL of concentrated nitric acid. An aliquot of the digested solution (0.5 mL) was diluted into 9.5 mL of NANOpure™ water. ICP standards were obtained from Inorganic Adventures and diluted using NANOpure™ water. Images were obtained using a JEOL 2010 transmission electron microscope (TEM) on ultrathin carbon type-A support film (Ted Pella).

2.3. Nanoparticle synthesis

The nanoscale magnetite was synthesised using a thermal decomposition reaction.[23,24] To iron (III) acetylacetonate (706 mg, 2.00 mmol), in a 100-mL round-bottomed flask with a stir bar, oleic acid (0.951 mL, 1.50 mmol), oleylamine (0.987, 1.50 mmol), 1,2-hexadecanediol (0.388 g, 3.00 mmol), and benzyl ether (37.5 mL) was added. The solution was heated to 200 °C under argon with constant stirring and held for 2 hours, before being heated to reflux and held for 1 hour. The solution was cooled to room temperature and then the nanoparticles were precipitated with ethanol (40 mL). The nanoparticles were centrifuged and washed with ethanol three times before air drying overnight, with a yield of 85%. The nanoparticles were then suspended in hexane (15 mL) in a 20-mL scintillation vial.

2.4. Magnetic measurements

Sand or CarboHSP was spread evenly into a 10.5” x 10.5” plastic tray, 0.5” deep. In the test, a 5 × 5 grid was prepared with 30, 60, 90, 120, and 150 μL of a nanoparticle solution (1.23 × 10⁻⁴ mmol Fe, 9.5 g/L) dropped into the five columns, respectively. Each row was a duplicate. The grid was covered with a layer of thin plastic wrap, so as to not contaminate the probe. The plastic wrap was first tested to see if there was any signal change; there was not. In addition, a beaker was filled with sand 1-cm deep. Nanoscale magnetite (30 μL) was added to the beaker and a measurement was taken. The probe was covered with a thin layer of plastic wrap. Then sand (0.1 cm) was added to the beaker and another measurement was taken, with the probe wrapped in a fresh layer of plastic wrap. Further 0.1-cm layers of sand were added and measurements were undertaken until a diamagnetic signal (indicating just sand) was obtained.
Quantification versus the proppant was determined by placing nMag (2.50 mL, 9.50 g/L) into each of two 20 mL scintillation vials. Sand was added to one vial until only a small amount of nanoscale magnetite solution was not covered. The same procedure was repeated with CarboHSP. In addition, an aliquot of nanoscale magnetite solution was diluted to both half and quarter concentration and then added to two 20 mL scintillation vials (2.50 mL; 4.75 g/L, 2.38 g/L, respectively). Sand and CarboHSP were added to the vials in the same manner as before. The relative quantities for each sample are given in Table 1. All four vials were placed in a fume hood, uncapped, to let the hexanes evaporate. Once there was no visible liquid, the vials were gently heated to ensure dryness (40 °C). After cooling, the contents of each of the vials was mixed thoroughly and then placed into a quarter of a segregated plastic Petri dish and spread out evenly. In addition, a comparable quantity of sand and CarboHSP was put into quarters of a segregated plastic Petri dish. The low field volume magnetic susceptibility of the mixtures was then measured with a handheld probe magnetic susceptibility device (an MS2E Sensor, by Bartington Instruments). The probe was zeroed between each data point. Both the background (air) and the sample (sand, CarboHSP, and sand/nanoparticle or CarboHSP/nanoparticle solution) measurement were recorded. Sand and proppant measurements were taken between each solution spot. Solution measurements were taken in the middle of the solution spot. It should be noted that volume magnetic susceptibility is unitless; however, we have used the notation ‘SI’ to indicate that the International System of Units was used in the calculation.

### 2.5. Magnetic measurements on shale core samples

Testing was conducted at Weatherford Laboratories (Houston, TX). Slabbed cores were supplied by Southwest Energy Company (Houston, TX). The two cores used in the experiments were the Harrison core from Faulkner County, Arkansas and the Rackley core from Cleburne County, Arkansas. The Harrison core had a total length of 359 feet (122 m), starting at a depth of 4240 feet (1445 m) and ending at 4599 feet (1567 m). The Rackley core had a total length of 713 feet (243 m), starting at a depth of 1970 feet (671 m) and ending at 2683 feet (914 m). Using the same handheld magnetic susceptibility probe as

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass of Unimin sand (g)</th>
<th>Mass of Carbo HSP (g)</th>
<th>[nMag] (g/L)</th>
<th>Magnetic susceptibility ($10^{-2}$ SI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.01</td>
<td>–</td>
<td>–</td>
<td>–0.20</td>
</tr>
<tr>
<td>2</td>
<td>–</td>
<td>11.02</td>
<td>–</td>
<td>25.7</td>
</tr>
<tr>
<td>3</td>
<td>10.12</td>
<td>–</td>
<td>2.38</td>
<td>37.6</td>
</tr>
<tr>
<td>4</td>
<td>8.91</td>
<td>–</td>
<td>4.75</td>
<td>80.1</td>
</tr>
<tr>
<td>5</td>
<td>11.16</td>
<td>–</td>
<td>9.50</td>
<td>179.3</td>
</tr>
<tr>
<td>6</td>
<td>–</td>
<td>9.18</td>
<td>2.38</td>
<td>52.3</td>
</tr>
<tr>
<td>7</td>
<td>–</td>
<td>10.37</td>
<td>4.75</td>
<td>121.4</td>
</tr>
<tr>
<td>8</td>
<td>–</td>
<td>12.11</td>
<td>9.50</td>
<td>214.6</td>
</tr>
</tbody>
</table>

Table 1. Summary of experimental quantities for nMag/proppant samples.
for the nanoparticles on sand experiment, measurements were taken by placing the handheld probe on the surface of the core at ambient temperature. On average, measurements were obtained every 4 feet. Some measurements were taken closer together, a few millimetres apart, when a large volume magnetic susceptibility was detected. Other measurements were much further apart, due to missing sections of the core. A background reading, the shale core volume magnetic susceptibility, and the corresponding depth were recorded. The instrument was zeroed every 48 feet and the detector was wiped, so as to remove any accumulation of material from the core. Visual variations in the composition of the cores can be seen in Figure 1.

3. Results and discussion
A typical magnetite nanoparticle (nMag) synthesis was chosen for the present studies involving the thermal decomposition of iron (III) acetylacetonate [Fe(acac)₃] in the presence of a suitable capping agent.[23,24] While we have shown that the identity of the surface functionalisation is important in controlling the mobility of a nanoparticle through a reservoir or proppant pack material,[9] in the present case an oleic acid functionality was chosen so that solutions in hexane could be prepared. The choice of hexane ensured that the solvent could be readily evaporated leaving the nMag dispersed upon the proppant material. Figure 2 shows the size distribution of the nMag to be within the range of 5–20 nm with an average of 11.8 nm, as determined by SAXS. This is consistent with the TEM image shown in Figure 3, which gives the particle size range of 6–23 nm and an average of 15 nm. Similar sized particles have been previously reported as MRI contrast agents.[11–16]
3.1. Detectability of nMag versus proppant

Two proppant materials were chosen for the study: sand and ceramic. To mimic a sand proppant pack, we have employed frac sand (Unimin, 20–40 mesh), which is high purity quartz sand produced from sandstone with smooth round grains (Figure 4(a)) between 300–600 μm in size and a sphericity of 0.6.[25] As a typical high strength ceramic, we used CarboHSP (20–40 mesh, 400–840 μm) with a supposed sphericity of 0.9, and a bulk density of 2.0 g/cm³ (Figure 4(b)). The composition of CarboHSP is Al₂O₃ (83%), SiO₂

![Figure 2. Size distribution obtained via SAXS of the magnetite nanoparticles in hexane (9.5 g/L).](image)

![Figure 3. Representative TEM image of the magnetite nanoparticles used in this study.](image)
(5%), TiO₂ (3.5%), Fe₂O₃ (7.0%), and other oxides (1.5%). The presence of iron oxide is expected to result in a significant magnetic susceptibility of the proppant, see below.

Since the core magnetic susceptibility measurements were conducted using a handheld magnetic susceptibility meter (see Section 2), it was appropriate that the same instrument be used for the proppant pack. Prior to investigating the detection limit (signal-to-noise) for the nMag against each proppant, we prepared a sample of nMag infused sand and measured the magnetic susceptibility as a function of the depth under the surface of fresh sand (see Section 2). The plot in Figure 5 shows that with the experimental set-up used, the measured detection is limited to the surface (or within <1 mm of the surface).

To determine how much nMag is needed in order to make a clear distinction between the two materials, a series of spots of a known volume of standard solution of nMag was deposited onto a uniformly packed sample of frac sand (Figure 6(a)). Varying amounts of magnetite nanoparticles (100–500 μL) of a standard solution (9.5 g/L, 1.23 × 10⁻⁴ mmol Fe) were added on top of a layer of uniformly packed sand (see Section 2). The resulting array would mimic the presence of the nanocontrast agent in the proppant pack at

![Figure 5](image)  
**Figure 5.** Plot of volume magnetic susceptibility of nMag (9.5 g/L)-infused Unimin sand as a function of the depth under the surface of fresh Unimin sand. See Section 2.4. for details.
different concentrations. The magnetic susceptibility of the array was measured in 1.5-cm increment measurements in order to determine the spatial resolution of the instrument. Figure 6(b) shows the associated plot of volume magnetic susceptibility as a function of distance for the array in Figure 6(a). Figure 6 shows the correlation between the position of the array and the magnetic susceptibility measurement.

Figure 6(b) shows that as expected from its high quartz content, the frac sand has a net negative magnetic susceptibility, due to its diamagnetism.[21,22] Furthermore, the usage of nMag with such proppant enables a clear distinction to be made between the two.

A similar set of measurements was made using a uniform pack of ceramic proppant. In this case, the magnetic susceptibility measurements (Figure 7) show that whilst there is a similar relationship of magnetic susceptibility with increasing concentration of the nMag...
the proppant itself is slightly paramagnetic \((25.7 \times 10^{-5} \text{ SI})\), consistent with the presence of iron oxide as a constituent.

In order to ascertain the relative quantity of nMag required for differentiation against each of the proppants, samples were prepared by infiltrating a known amount of nMag solution into a known amount of proppant (see Section 2). Using the magnetic susceptibility data in Table 1, it is possible to determine the concentration dependency of the magnetic susceptibility, as shown in Figure 8. These relationships can be used to determine the concentration of nMag that must be present to be able to differentiate nMag within the proppant pack.

The concentration required for the detection of nMag against a proppant pack can be estimated assuming that the magnetic susceptibility needs to have a value that can be differentiated from the proppant. For example, the magnetic susceptibility of sand is \(-0.2 \times 10^{-5} \text{ SI}\) and we can assume that a signal of \(+0.2 \times 10^{-5} \text{ SI}\) can be readily differentiated. From Figure 8, we can calculate the concentration of nMag must be 0.269 g/L. In a similar manner, if it is assumed that in the case of CarboHSP a signal of 50% greater than the background is needed, then a concentration of nMag of 1.01 g/L is required. Given these numbers, we can estimate the quantity of nMag as a function of the particle concentration as compared to either the mass of proppant (sand or CarboHSP) or the volume of frac fluid used (Table 2).

Based upon the mass of proppant used (Table 1) we can estimate the amount of nMag required for each type of proppant (Table 2). Given that the cost of proppants vary...
between $0.22/kg (sand, $0.10/lb) and $1.32/kg (ceramic, $0.60/lb), and that we can estimate the raw material costs for nMag to be ca. $13,600/kg, the added cost ($0.9/kg sand or $3/kg ceramic) would be a significant increase over the proppant costs.

In a typical vertical well, ca. 220,000 kg (100,000 lbs) of proppant are used. In contrast, a multi-stage frac job will use approximately 440,000–660,000 kg of proppant per stage, resulting in a total consumption as high as 5.4 million kg (12 million lbs). Thus, if we assume a value of 440,000 kg (200,000 lbs) for a single stage, the amount of nMag required to allow detection above the background of the sand proppant is calculated from Figure 8 to be 29.6 kg (13.4 lb). In the case of a ceramic proppant, such as CarboHSP, this value would be 101 kg (45.8 lb). With a multi-stage frac job, a total amount of nMag could be as high as 4000 kg.

The estimates above are based upon the relationship of the nMag to the proppant placed in the frac. However, this mass of proppant is placed using a large volume of water (frac fluid) and the proppant does not go to all the areas that are fractured. Thus, we need some estimation of the amount of nMag that would be required to maintain a concentration sufficient for detection based on the volume of water used in the frac fluid. In Texas, estimates of water use for hydraulic fracturing vary from 10,600 m$^3$ (2.8 million gallons) to 21,500 m$^3$ (5.6 million gallons) per well.[26] Taking a value of 3 million gallons and the concentration required, an estimate of the amount of nMag needed for a well based upon the frac fluid volume can be estimated, see Table 2.

### 3.2. Detectability of nMag versus shale gas reservoir rock

In the forgoing discussion, we were simply concerned with the detection of nMag against a background of the proppant (Figure 9(a)) that creates a pack to maintain permeability of the well. However, the detection of nMag in the borehole will be against a background of not only the proppant, but also the oil/gas, connate fluids, and the reservoir rock itself (Figure 9(b)). We have previously shown that the petroleum reservoir fluids have a range of components for which the mass susceptibility may be measured;[27] however, their contributions will be lower than that of the proppant or the source rock.[21] In order to ascertain the levels of nMag required to provide a contrast with the reservoir rock, we...
have measured the magnetic susceptibility of two shale cores (see Section 2): Harrison (Faulkner County, AR) and Rackley (Cleburne County, AR). Both are typical shale gas well reservoirs.

Figure 10 shows the volume magnetic susceptibility of the core as a function of the reservoir depth. It is clearly seen that the reservoir rock is generally paramagnetic rather than diamagnetic as a function of the mineral composition of typical shales. Paramagnetic clays, like illite \((\text{K, H}_2\text{O})(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]\), show a small, positive magnetic susceptibility, while iron bearing paramagnetic minerals like siderite \((\text{FeCO}_3)\) have higher positive magnetic susceptibilities. A small concentration of a ferrimagnetic mineral would also give a significant positive magnetic susceptibility. For both shale cores, there appears a representative background level of the magnetic susceptibility of ca. \(45 \times 10^{-5} - 50 \times 10^{-5}\) SI. However, there are regions that have magnetic susceptibilities of \(>200 \times 10^{-5}\) SI (see Figure 10). These regions could be due to higher concentrations of ferrimagnetic particles or due to regions of a paramagnetic mineral like siderite.

Figure 10. Plots of volume magnetic susceptibility \((10^{-5}\ \text{SI})\) for (a) Harrison and (b) Rackley shale cores as a function of the reservoir depth (m). Note: The concentration of nMag (g/L) required for a particular magnetic susceptibility is shown along with background and peak values of the shale cores (dashed lines).
Using the quantitative data discussed above, we can calculate the quantity of nMag required to differentiate from a representative background and the peak values (Figure 10). The results are given in Table 3. A comparison of the concentrations required to be added to a frac fluid in order to differentiate the nMag from the reservoir rock is significantly higher than that needed to differentiate from the proppant. Between $8.64 \times 10^4$ and $2.43 \times 10^5$ kg per well would be needed with a cost of $1\text{ billion per well.}$

### Table 3. Summary of estimated nMag required for detection above the reservoir rock.

<table>
<thead>
<tr>
<th>Level of reservoir magnetic susceptibility</th>
<th>Conc. nMag for differentiation from reservoir rock (g/L)</th>
<th>nMag required (kg/kg proppant)</th>
<th>nMag required for 2 $\times$ $10^5$ lb frac stage (kg)</th>
<th>nMag required for 3 $\times$ $10^6$ gal frac (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background</td>
<td>1.56</td>
<td>$3.91 \times 10^{-4}$</td>
<td>172</td>
<td>$8.64 \times 10^4$</td>
</tr>
<tr>
<td>Peak</td>
<td>13.2</td>
<td>$3.29 \times 10^{-3}$</td>
<td>1450</td>
<td>$2.43 \times 10^5$</td>
</tr>
</tbody>
</table>

*aSee Figure 10 for susceptibility values as compared to the reservoir rock.

bValues calculated from Figure 8.

c1 lb = 0.454 kg.

### 4. Conclusions

It is clear that while the quantities of the nMag are high as compared to biomedical applications, this work has demonstrated such materials could theoretically be used as contrast agents in shale gas reservoirs. The particles could be pumped into the well with the fracturing fluid and detected in the well via a volume magnetic susceptibility detector, similar to the one used in the above experiments. Unfortunately, the biggest issue would be the high cost of the quantities required. Two solutions to this are possible. First, the cost predictions used herein do not take into account either costs of manufacture of the nMag (which would increase the cost) or the lowering of costs through bulk manufacturing methods and alternative (cheaper) starting materials; only the cost of the starting materials used were calculated. Thus, significant lowering of costs would clearly be beneficial. Second, it would be useful for any downhole contrast agent to have an even higher magnetic susceptibility than nMag and particularly a higher magnetic susceptibility at downhole reservoir temperatures. It would be especially useful if the magnetic susceptibility were temperature independent across the range of temperatures experienced downhole. Thus, as the susceptibility of the reservoir rock and/or the proppant decreases with increasing temperature,[22] the signal-to-noise will be enhanced. In this regard, the superparamagnetic mixed oxide spinels, $\text{Mn}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$, are known to have a higher magnetic susceptibility than magnetite making it an ideal candidate and worth further investigation.[28]

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