MAGNETIC NANOPARTICLES FOR THERMALLY ANOPARTICLES ENHANCED HEAVY OIL RECOVERY

Hazem Elshorbagy Elshorbagy

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MAGNETIC NANOPARTICLES FOR THERMALLY ENHANCED HEAVY OIL RECOVERY

Hazem Elshorbagy

This thesis is submitted in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering

Under the Supervision of Professor Yousef Haik

January 2014
Declaration of Original Work

I, Hazem Elshorbagy, the undersigned, a graduate student at the United Arab Emirates University (UAEU) and the author of the thesis titled “Magnetic Nanoparticles for Thermally Enhanced Heavy Oil Recovery”, hereby solemnly declare that this thesis is my original research work which was carried out under the supervision of Prof. Yousef Haik, in the College of Engineering at UAEU. This work has not been previously formed as the basis for the award of any degree, diploma or similar title at this or any other university. The materials borrowed from other sources and included in my thesis have been properly cited and acknowledged.

Student’s Signature: _________________________ Date: _________________________
Abstract

A novel method of delivering thermal energy efficiently to reservoirs for heavy oil production is described in this study. The method uses magnetic nanoparticles that generate heat locally when exposed to a high frequency magnetic field oscillation via hysteresis losses. This concept is currently used in medical research to thermally kill cancerous cells. Electromagnetic heating is an alternative method to heat heavy oil reservoirs without using water or steam. Using magnetic nanoparticles with electromagnetic heating would greatly reduce the energy requirement and would allow efficient propagation of heat into deeper regions beyond wellbore locality that are otherwise difficult to reach.

In this study, an alternating magnetic field is used to heat different types of dry and water dispersed nanoparticles and the temperature rise over time was measured. Two types of nanoparticles (NPs) generated the most amount of heating; pure Iron III Oxide (Fe$_3$O$_4$) and Fe$_3$O$_4$ mixed with Erbium (Er) in a 75% to 25% chemical ratio (Fe/Er 75-25). Fe$_3$O$_4$ and Fe/Er 75-25 samples were then prepared for different sizes and chemical compositions and were characterized for size using a nanosizer and Scanning Electron Microscope (SEM) images, morphology using X-ray Diffraction (XRD) analysis, chemical composition using Energy Dispersive Spectrometer (EDS) and hysteresis loop using a Super-conducting Quantum Interference Device (SQUID) test. Bitumen was used to simulate heavy oil conditions in which the nanoparticles were dispersed to create a nano ferro-fluid. The particles were then dispersed in bitumen samples and the effect of varying concentration, particle size and chemical ratio (50% and 75% Erbium) on
heating efficiency was examined. The tested particle sizes were in the range of 40-120nm which means they were all above the critical size for superparamagnetism (~27nm for the particle investigated in this study) and hence all heating generated by the NPs was attributed to hysteresis losses.

Characterization revealed high crystallinity of pure Fe$_3$O$_4$ samples and a tendency of crystallinity to decrease as the percentage of Erbium added to Fe$_3$O$_4$ is increased. SEM images revealed a tendency of the particles to aggregate as the percentage of Erbium increased. Except for Fe/Er 75-25, heating experiments revealed a negative relationship between concentration of NPs and Specific Absorption Rate (SAR); as concentration of NPs increased the SAR decreased. For NP size, the results followed a common trend; SAR increased when NP size was decreased. In terms of chemical composition, it was revealed that the optimal percentage of Er added to Fe$_3$O$_4$ to enhance its heating capability was 25% whereas any increase in Er % beyond that point caused a proportional decrease in SAR.

Keywords: magnetic nanoparticles, superparamagnetism, specific absorption rate, nanosizer, x-ray diffraction, bitumen.
استخدام جزيئات النانو لتحسين التسخين المغناطيسي في استخراج النفط الثقيل

هذه الدراسة تهدف إلى وصف طريقة جديدة لإيصال الطاقة الحرارية بكفاءة أثناء عملية إنتاج النفط الثقيل. يستخدم الأسلوب مبدأ التدفئة المغناطيسية التي تولد الحرارة محلياً عندما تتعرض جزيئات النانو لمجال التدبيب المغناطيسي وذلك عن طريق خسائر التباعد. يستخدم هذا المفهوم حالياً في مجال الأبحاث الطبية لقتل الخلايا السرطانية حرارياً.

التدفئة الكهرومغناطيسية هي طريقة بديلة لتسخين خزانات النفط الثقيل دون استخدام الماء أو البخار. إن استخدام الجسيمات النانوية المغناطيسية مع التدفئة الكهرومغناطيسية يقلل كثيراً من متطلبات الطاقة ويسهم بنشر فعال للحرارة إلى مناطق أعمق في أبار النفط الثقيل والتي يصعب الوصول إليها حالياً.

في هذه الدراسة، تم استخدام المجال المغناطيسي لتسخين أنواع مختلفة من الجسيمات النانوية وتم قياس ارتفاع درجة الحرارة مع مرور الوقت. نوعين من الجسيمات النانوية ولدا أكبر قدر من التدفئة، الحديد III أكسيد (Fe<sub>3</sub>O<sub>4</sub>) و مختلطة مع مادة الأربيوم (Er) بنسبة المواد الكيميائية 75% إلى 25% (25-75). تم تحضير عينات باختلاف حجمها وتركيب كيميائي متغيرة ثم تم تشخيص جميع العينات باستخدام تقنيات المختبر كالتالي: تحديد الحجم باستخدام جهاز الـ SEM والمسح الضوئي الإلكتروني، والمجهرية (nanosizer) الجسيمات المتغيرة لوحجة XRD، واختبارات كيميائية باستخدام حيوت الأشعة السينية (EDS).

تم استخدام البيتونين لمحاكاة ظروف النفط الثقيل حيث أضيفت الجسيمات النانوية إلى سائل البيتونين (bitumen) لخلق تركيبة النانو السائل. تم دراسة تأثير تفاوت تركيز جسيمات النانو، وحجم الجسيمات، والنسب الكيميائية للإربيوم (Er) على كفاءة التدفئة. وقعت أحمام الجسيمات التي تم اختبارها في مجال الـ 40-120 nm وهو ما يعني أنهم كانوا جميعاً فوق الحرم لجزيئات النانو (superparamagnetism) وبالتالي تم عزل كل التدفئة التي ولدتها جسيمات النانو إلى خسائر التباعد (hysteresis).
كشفت نتائج التوصيف (SEM+XRD) ميل جسيمات النانو إلى التراكم وانخفاض معدلات التبلور عند زيادة نسبة الاربيوم (Er) المضافة إلى الحديد (Fe). باستثناء 25-75%Fe/Er, كشفت تجارب التسخين الكهرمغناطيسي وجود علاقة سلبية بين تركيز جسيمات النانو في سائل البيتومن ومعدل الامتصاص النوعي (SAR). كما أظهرت النتائج زيادة في معدل الامتصاص النوعي (SAR) عند انخفاض حجم جسيمات النانو. اما بالنسبة للتركيب الكيميائي، تم الكشف عن أن النسبة المثلثة للاربيوم (Er) التي تولد أعلى معدلات ارتفاع الحرارة والامتصاص النوعي هي 25% في حين أن أي زيادة ما بعد تلك النقطة تسبب انخفاض نسبي في الفاعلية الحرارية.
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I would like to thank my advisor, Professor Yousef Haik for his unwavering support and enthusiasm throughout this research endeavor. Our discussions of research ideas allowed me to come up with this unique idea that crosses between many different hot areas of research and involves a lot of multidisciplinary topics that greatly reinforced my academic knowledge and professional expertise. I would also like to deeply thank Eng. Tahir Abdulrahman for generously helping me prepare and characterize the nanoparticles and set up the experimental apparatus. Many thanks to all engineers and lab technicians across the Mechanical Engineering, Electrical Engineering and Physics departments that provided me with the necessary equipment and guidance including Eng. Muthana Aziz, Eng. Asma Al Hati, Eng. Abdulrahman, Eng. Ahmed Abd-Rabou, and Eng. Mohammed El Shaer. My deepest gratitude to Mariam Al Kaabi, the Office of Graduate Studies and the Mechanical Engineering Department at UAEU for being patient and supportive during my Masters and Thesis. Finally, I warmly thank my family and friends for their immense support and motivation that they have provided me that helped bring the best out of me towards my educational and professional journeys.
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**Acronyms and Abbreviations**

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<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>API</td>
<td>American Petroleum Institute gravity</td>
</tr>
<tr>
<td>Br</td>
<td>Remanence (emu/g)</td>
</tr>
<tr>
<td>cP</td>
<td>Centipoise</td>
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<tr>
<td>CSS</td>
<td>Cyclic Steam Stimulation</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
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<tr>
<td>EM</td>
<td>Electromagnetic Heating</td>
</tr>
<tr>
<td>EOR</td>
<td>Enhanced Oil Recovery</td>
</tr>
<tr>
<td>ESD</td>
<td>Energy Dispersive Spectrometer</td>
</tr>
<tr>
<td>Hc</td>
<td>Coercivity (Oe)</td>
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<td>M</td>
<td>Magnetization</td>
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<td>MNH</td>
<td>Magnetic Nanoparticle Heating</td>
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<td>Magnetic Nanoparticles</td>
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<td>NP</td>
<td>Nanoparticles</td>
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<tr>
<td>( \omega )</td>
<td>Angular Frequency</td>
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<tr>
<td>PVC</td>
<td>Poly Vinyl Chloride</td>
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<tr>
<td>PWM</td>
<td>Power Pulse-width Modulator</td>
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<tr>
<td>SAGD</td>
<td>Steam Assisted Gravity Drainage</td>
</tr>
<tr>
<td>SAR</td>
<td>Specific Absorption Rate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<tr>
<td>SLP</td>
<td>Specific Power Loss</td>
</tr>
<tr>
<td>SOR</td>
<td>Residual Oil Saturation</td>
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<tr>
<td>SQUID</td>
<td>Super-conducting Quantum Interface Device</td>
</tr>
<tr>
<td>TB</td>
<td>Blocking Temperature</td>
</tr>
<tr>
<td>T</td>
<td>Relaxation Time-constant</td>
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<tr>
<td>-------</td>
<td>--------------------------</td>
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<td>XRD</td>
<td>X-ray Diffraction</td>
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Chapter 1: Introduction

1.1 Problem Statement

With the continuous depletion of the world's supply of conventional oil, there is an increasing demand for exploiting unconventional oil and gas resources. In this market, heavy oil production has gained a lot of importance in recent years due to enormous reserves that exist in the various parts of the world such as Canada, US, Venezuela, Russia and the Middle East. Carbonate rocks cover over 20% of the earth’s crust and they contain over 20% of the world's endowment of viscous oil estimated at over 2 trillion barrels. In the Middle East alone, heavy oil in fractured carbonate reservoirs accounts for 25–30% of the total oil in place in the region (Nabipour, 2007). The largest deposits of oil or tar sands are found in Canada and Venezuela, which have combined oil sand reserves estimated to be equal to the world’s total reserves of conventional crude oil. Canada’s tar sands now provide the U.S. with more than one million barrels of oil a day.

The difficulty in producing heavy oil is owed to its high viscosity and specific gravity due to which its ability to flow within the reservoir is low. Steam injection, known as steam assisted gravity drainage (SAGD), is the most common and effective recovery method. In SAGD, the steam is used as the heat carrier to increase the temperature and reduce the viscosity of heavy oil, and consequently reduce the flow resistance of heavy oil through porous media which increases the yield and production rate. Despite this, heavy oil recovering and upgrading has been proven to be economically expensive as well as environmentally unfriendly. Extraction and separation of bitumen for the purpose of processing to fuels is much more expensive than extracting conventional oil
by drilling and involves the use of significant amounts of energy and water. The environmental problems associated with extracting oil using SAGD are now a source of considerable concern primarily due to the risk of contamination of vast quantities of fresh water. In addition, steam generation consumes large amounts of natural gas and leads to higher CO₂ emissions, which impacts profitability of the SAGD operation and the environment in a negative way. Moreover, there are other technical challenges associated with steam injection such as accelerated well corrosion leading to internal blowouts of hot fluids, or risk of blowout to surface because of stress changes and shale shrinkage, especially with shallow steam projects. These problems, illustrate the urgent need to develop a new technology to recover viscous oil.

Electromagnetic heating is an alternative method to heat heavy oil reservoirs without using water or steam. The problem of electromagnetic heating is that it requires large amounts of energy and it cannot reach all regions of the reservoir effectively. Therefore, using nanoparticles to assist the electromagnetic heating presents huge potential. Magnetic nanoparticles are expected to reduce the energy requirement given their magnetic nature and their small size would allow them to travel to deeper regions beyond wellbore locality.

1.2 Heavy Oil Overview

Global oil supplies have steadied and are slowly decreasing while demand for liquid fuels continues to rise. Conventional crude oil is forecasted to account for only 60 percent of liquid-fuel supply by 2040, a drop from 80 percent in 2010. This supply gap is anticipated to be filled by an array of new unconventional oils. Unconventional oils are those obtained by non-traditional production techniques because they cannot be
recovered through pumping in their natural state. These are divided into four types: heavy oil, extra heavy oil, bitumen, and oil shale (Gordon, 2012).

"Heavy" oil refers to oil that contains high amounts of sulfur and other components causing it to be very dense. Because of its high viscosity, heavy oil is generally more expensive to extract from the ground and refine into gasoline. The U.S. Geological Survey estimates that there are 3 trillion barrels of heavy oil scattered around the earth – worth about 100 years of consumption – but only about 400 billion barrels are recoverable with today's existing technology. It is evident from the map below that the Middle East, North America and South America hold the majority of these deposits while Saudi Arabia alone is estimated to have 78 billion barrels of recoverable heavy-oil reserves (Holmes, 2011).

![Figure 1: Estimated heavy-oil deposits by region (Source: U.S. Geological Survey, 2011)](image)

Improved oil recovery (IOR), is a general term which refers to improving oil recovery by any means while Enhanced Oil Recovery (EOR) is a more specific term that implies a reduction in oil saturation below the residual oil saturation (Sor). EOR is usually
associated with the tertiary recovery stage which targets immobile oil whereas primary and secondary recovery stages deal with mobile oil. EOR can be performed by any of the following mechanisms; (a) a reduction of oil viscosity, (b) use of a solvent to extract the oil, and (c) alteration of capillary and viscous forces between the oil, injected fluid, and the rock surface. There are three types of EOR methods; thermal (injection of heat), miscible gas injection methods (injection of a solvent) and chemical methods (injection of chemicals/surfactants).

Thermal methods are the most common and well developed among EOR methods, as far as field experience and technology are concerned. They are best suited for heavy oils (10-20° API). Thermal methods supply heat to the reservoir, and vaporize some of the oil causing a large reduction in viscosity, hence reducing the mobility ratio. Cyclic Steam Stimulation (CSS), steam flooding, and Steam Assisted Gravity Drainage (SAGD) rely on the injection of hot steam to lower oil viscosity, while in situ combustion injects air or oxygen to burn a portion of the in-place oil to generate heat (Thomas, 2007).

The most popular method for heavy oil recovery is SAGD, however, the environmental problems associated with extracting oil using SAGD are now a source of considerable concern primarily due to the risk of contamination of vast quantities of fresh water. In addition, steam generation consumes large amounts of natural gas and leads to higher CO₂ emissions, which impacts profitability of the SAGD operation and the environment negatively. Moreover, there are other technical challenges associated with steam injection such as accelerated well corrosion leading to internal blowouts of hot fluids, or risk of blowout to surface because of stress changes and shale shrinkage, especially with shallow steam projects.
These immense environmental drawbacks of steam flooding have greatly hindered the potential of heavy oil exploitation due to many governmental restrictions as is the case with Canada’s oil sands. Other heating alternatives that do not require steam are alternatively being considered. Electrical heating for instance, is being used to heat the high-viscosity oil in heavy oil reservoirs for its enhanced recovery (Hascakir, 2008). Inductive heating of the heavy oil reservoirs has also been investigated and tested. The latter technique heats reservoirs by oscillating water molecules in the reservoir which locally heats the fluids. Disadvantages of these electromagnetic (EM) methods include an uneven distribution of heating due to sparse water saturation, and poor propagation of heat beyond the wellbore (Sierra, 2001).

This study focuses on electromagnetic heating enhanced by use of nanoparticles as a thermal EOR method that displaces oil by reducing viscosity of heavy oil as a cleaner alternative to problematic steam injection processes.

1.3 Hyperthermia Overview

Hyperthermia has been proposed for locally increasing tissue temperature for potential therapies for diseased tissue. It was first proposed for cancer treatment (Herrera, 2006). In the process, cancer cells are killed by increasing their temperature above 43 – 45 °C, the minimum protein denaturation temperature (Roti Roti, 1998). Hyperthermia involves injecting magnetic particles into the ill organ or tissue and exposing these particles to an electromagnetic field which stimulates heat generation from the particles. This treatment approach was first introduced in the 1940’s by Gilchrest et al. when a medical warning announced that metallic objects within the body were heated upon exposure to a magnetic field. The leading-edge work of Gilchrest’s team at the time led to a wide scale
research effort across the world to study the potential of hyperthermia as a viable means of cancer treatment.

The development of nanotechnology over the past 20 years has greatly contributed to the effectiveness of hyperthermia techniques as nanoparticles (NPs) enhanced the ability to locally heat cancerous tissue in a highly controlled manner (Batlle, 2002), (Hergt, Physical Limits of Hyperthermia Using Magnetite Fine Particles, 1998). The successful use of NPs for hyperthermia in the medical industry has led to recent studies to apply the same concept to overcome the limitations of electromagnetic (EM) heating in heavy oil applications and make it a strongly viable alternative to steam flooding processes.

The major advantage of nanoparticle EM heating is that it can be carried out in the absence of water. The nanoparticles can be selectively placed in regions where heat is necessary, and stimulated to generate the desired amount of heat in a controlled manner. The general principles underlying how the nanoparticles convert magnetic energy to heat are discussed in subsequent sections of this thesis. The advantage of this technique is that the heat-generating nanoparticles are in direct contact with the targeted fluid, so fast and efficient conductive heating can take place. Furthermore, the EM energy necessary to stimulate the nanoparticles can be directed to the desired locations via a waveguide allowing the propagation of heat beyond wellbore locality (Davidson, 2012).

1.4 Research Objectives

This project is listed under the efforts required to evaluate the feasibility of employing magnetic nanoparticles that are responsive to external electromagnetic stimuli and able to generate heat to be utilized for in situ thermal recovery of heavy oil. The objectives of this study are to:
1. Evaluate hyperthermia characteristics of different formulations of ferrite based nanoparticles.

2. Synthesize nanoparticles with different formulations and sizes, test the NPs and evaluate the effect of size, chemical composition and concentration on amount of heat produced.

3. Relate experimental results to theoretical models and results from literature.

The final outcome is a recommendation for the most efficient nanoparticle types and conditions required to maximize heat production for heavy oil recovery. The results will serve as technical proof that using magnetic nanoparticles along with electromagnetic energy instead of SAGD results in higher oil production for less energy consumption.

1.5 Research Scope

This investigation was conducted to determine the effectiveness of using magnetic nanoparticles for electromagnetic heating during heavy oil recovery. Nanoparticles selected were of ferrite nature and were synthesized and characterized using UAE University’s lab facilities and equipment. The nanoparticle properties characterized were particle size, morphology, chemical composition and hysteresis loop behavior. Locally purchased bitumen was used to simulate heavy oil conditions and 10ml test tubes were used as the medium for sample testing. Heat production was estimated using SAR calculation based on the measured temperature-time profile and mass of fluid-nanoparticle mixture. The effect of nanoparticles’ chemical composition, concentration and particle size on SAR is studied and compared to relevant literature.

The thesis consists of 6 chapters divided as follows:
• Chapter 1 serves as an introduction that clarifies the problems addressed by this study and the market potential the solution presents.

• Chapter 2 presents the theoretical background required to understand the experimental work and results of the study. Major topics include understanding of magnetic nanoparticles heating modes, the properties that are important for heating and calculations used for analysis.

• Chapter 3 describes the procedures used to prepare the different types of nanoparticles, the processes and results deployed to characterize them for size, morphology, chemical composition and magnetic coercivity.

• Chapter 4 deals with the experimental coil setup used to electromagnetically heat the samples, the general temperature-viscosity relationship of heavy oil, and the results of heating the MNP dispersed in bitumen samples in terms of temperature-time profiles.

• Chapter 5 deals with thorough analysis of the collected results which examines the effect of each of the variables (NP size, NP concentration and chemical composition) on temperature rise and SAR. The results are explained by theories presented in the literature section (Chapter 2).

• Chapter 6 presents a well-rounded conclusion of all the work described in the thesis and the recommendations for future work that can be done to continue efforts in the direction MNP aided EM heating for heavy oil recovery.
Chapter 2: Theoretical Background

This chapter discusses the theory that relates to the experimental work conducted. It explains the concept of magnetic nanoparticle heating (MNH), the different types of nanoparticles, the mechanisms by which magnetic nanoparticles (MNPs) generate heat, and the properties that affect the amount of electromagnetic heating generated.

2.1 Relevant Magnetic Principles

Magnetic nanoparticle heating (MNH) takes place based on certain magnetic principles. Initially, the magnetic energy must be generated which is achieved experimentally by running AC current through a solenoid. A solenoid consists of a number of wire turns that allow current to flow in a circular direction generating a magnetic field. The field propagates perpendicular to current flow and is maximum at the center, while it reduces to zero at the external surface of the wire (Kong, 1986). The magnetic field induced within the solenoid can be calculated using Ampere’s law shown in Eq. (1).

\[ B = \frac{\mu NI}{L} \]  

where \( B \) is the induced magnetic field [T], \( \mu \) is the relative magnetic permeability of the material [dimensionless], \( N \) is the number of solenoid wire turns, \( I \) is the current flowing through the wire turns [A], and \( L \) is the axial length of the solenoid[m]. If the magnetic field strength, \( H \), is known, the induced magnetic field can be calculated as follows:

\[ B = \mu_0(H + M) \]  

\[ H = \mu B \]  

where \( \mu_0 \) is the magnetic permeability of free space \([4\pi \times 10^{-7} \text{ H m}^{-1}]\), \( H \) is the magnetic field strength (amplitude) \([\text{A m}^{-1}]\), and \( M \) is the magnetization of the material \([\text{A m}^{-1}]\).
When a magnetic material is placed in the electromagnetic field induced inside a solenoid, a heating stimulus is generated inside the material. The amount of heat generated depends on the type of magnetic material used. Paramagnets behave as magnets and have a magnetic moment in the same direction of the applied magnetic field, but as soon as the current flow is stopped, paramagnets lose their magnetism (Morrish, 2001). Diamagnets induce magnetic moments in the opposite direction of the magnetic field; however, once the field is removed, they lose magnetism. Ferromagnets are comprised of domains of free electrons such that when exposed to a magnetic field, the spins of free electrons align, thus inducing permanent magnetism within each domain (Callister, 2007). Within the ferromagnetic material, each domain has a randomly different spin alignment direction from the other, causing the net magnetic moment to be naturally small. However, the magnetic moments of all domains align when exposed to a magnetic field generating a larger magnetization than for other types of magnetic materials. This larger magnetization amplifies the overall magnetization and the amplification effect is known as the relative permeability of the material which depends on the magnetization strength of the material (Davidson, 2012).

In this work, the types of materials of interest are ferromagnetic and superparamagnetic magnetic nanoparticles. Magnetic nanoparticles (MNPs) are a class of nanoparticle which can be manipulated using magnetic field and are smaller than 1 micrometer in diameter (typically 5–500 nanometers). The minimum size of magnetic domains in ferromagnetic NPs is around 20nm below which the material cannot be split into further domains and thus exist as single domain particles. When the magnetic nanoparticle (MNP) is in a single domain size (below 20nm) and its temperature is above a particular temperature known as the blocking temperature (TB), it is described as superparamagnetic. In a
superparamagnetic state, the magnetic moments of the NPs fluctuate randomly generating a continuously fluctuating and large magnetic moment. When a magnetic field is applied, superparamagnetic MNPs respond quickly to the changes of the magnetic field because they have zero remanence (residual magnetization) and coercivity (the magnetic field required to bring the magnetization back to zero) (Gubin, 2005). Since they have zero remanence and coercivity, magnetic hysteresis, a certain heating phenomenon, will not occur in superparamagnetic NPs (Bashar Issa, 2013). Other than hysteresis, different types of relaxation modes contribute to the heating effect generated in ferromagnetic and superparamagnetic NPs which will be further discussed in the next chapter.

2.2 Nanoparticle Heating Modes

MNPs generate heat by one of three mechanisms: Neel relaxation, Brown relaxation, and hysteresis. The dominant heating mechanism is dictated mainly by the alternating current (AC) frequency of the applied electromagnetic energy as well as the size of the nanoparticles. The frequency determines if the particle is being heated through Neel or Brown relaxation modes, while size determines if the particles dissipate heat by a relaxation mechanism or hysteresis.

Brownian relaxation occurs when the magnetic moment of the particle is locked to the easy axis, such that a change in the magnetic field results in the particle physically rotating. Heat is generated as a result of the friction induced by the particle rotation. As the viscosity of the fluid increases, particle rotation becomes obstructed; therefore, Brownian relaxation is not considered in this study as we deal with highly viscous oil. The figure below illustrates the mechanism by which Neel and Brownian relaxations occur:
In Neel relaxation the particle remains stationary as the magnetization vector rotates with respect to the particles’ easy axis (Ming Ma, 2003). Neel relaxation time is calculated as follows

\[ \tau_N = \tau_0 e^{\frac{kV}{kT}} \]  

(4)

where \( \tau_N \) is the Neel relaxation time [s], \( \tau_0 \) is the pre-exponential factor [s], \( k \) is Boltzmann’s constant \( [1.3806503 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}] \), and \( T \) is the measurement temperature [K]. The pre-exponential factor is a measure of a particle’s anisotropic energy and is a function of variables such as the anisotropic constants, temperature, saturation magnetization, and height of energy barrier among others. The pre-exponential factor is generally considered a constant in the range of \( 10^{-9} – 10^{-13} \text{s} \), and has been found to be \( \sim 10^{-9} \text{s} \) for iron oxide nanoparticles (Neel, 1949) and (Moskowitz, 1997).

The relaxation time of the Brownian motion is calculated via Eq. (5)
where $\tau_B$ is the Brown relaxation time [s], $\eta$ is the viscosity of the fluid [Pa-s], and $r_h$ is the hydrodynamic radius of the particles [m].

The effective time constant computes the combined effect of both Brownian and Neel relaxation which is calculated using Eq. (6).

$$\frac{1}{\tau} = \frac{1}{\tau_N} + \frac{1}{\tau_B} \quad \text{(6)}$$

Researchers have also demonstrated that the dominant relaxation mechanism is also dependent on the AC frequency of the magnetic field. Fig. 2 demonstrates the results of an experiment performed by (Hergt, Maghemite nanoparticles with very high AC-losses for applications in RF-magnetic hyperthermia, 2003).

---

Figure 3: Frequency dependence of specific loss power deduced from the measured imaginary part of susceptibility for original ferrofluid (a) and suspension gel (b)
The figure indicates that the ferrofluid has a larger specific loss power (SLP) in the frequency range of 10 Hz – 100 kHz, where the sample is in fluid phase which demonstrates that Brownian relaxation was the dominant relaxation mechanism. At a frequency of 100 kHz the ferrofluid and gel curves merge together, which is the point at which Neel relaxation begins to dominate. For experiments and applications where the NPs are embedded in a solid media, it is recommended to maintain the frequency above 100 kHz in order to observe contribution from Neel relaxation.

Another loss mechanism that is not characterized by NP relaxation is hysteresis which is the primary focus in this study. As mentioned previously, hysteresis does not occur in superparamagnetic nanoparticles, but experiments reveal that hysteresis is dominant in larger particles (above 20nm). Furthermore, hysteresis is an important consideration if particles with a large size distribution are in the sample. Hysteresis losses occur due to the presence of domain walls in multi-domain ferromagnetic particles. As the particles are magnetized and demagnetized, a lag occurs between applied and induced magnetic field which results in a hysteresis loop. This coincides with the nature of large ferromagnetic particles in terms of possessing properties of coercivity and remanence. This means that a coercive force is required to demagnetize the particles and a residual magnetization remains once the magnetic field is removed. This cycle of continuously magnetizing and demagnetizing the particles causes their magnetic domains to expand and contract due to movement of their domain walls. This movement of domain walls against each other produces friction, which dissipates heat (Kronmuller, 2003).
amount of energy dissipated per magnetization/demagnetization cycle can be calculated by integrating the area of the hysteresis loop (Bertotto, 1998), (Davidson, 2012).

2.3 Nanoparticles Properties Important for Heating

There are certain properties that affect the amount of heat dissipated by magnetic nanoparticles through either of the three heating mechanisms; Brownian, Neel or hysteresis heating. Heat is usually generated by placing the magnetic particles in a magnetic coil that produces a magnetic field and excites the particles thus generating heat. This section will discuss the most important properties and how they affect the amount of heat produced. The amount of heat produced is usually measured in terms of Specific Absorption Rate (SAR) which is a calculation that estimates the amount of heat energy dissipated per unit mass of nanoparticles.

*Applied magnetic field*

The applied magnetic field plays a major role in determining the amount of magnetic energy dissipated by the magnetic coil, hence the amount of heat generated in the medium. Two primary properties are used to characterize a magnetic field; the frequency of the field and its amplitude.

Theory has proven that magnetic hyperthermia is proportional to the square of the applied magnetic field amplitude. Experimentally, this correlation has been validated as it has been shown that SAR generally increases with increasing field strength.

Experiments also showed that frequency has a more complex relationship with SAR compared to field amplitude. However for the frequency range of 100 to 300 kHz, the
effect of frequency was seen to be subtle. Magnetic field frequency proves to play a defining role on the optimal radius for generating heat from the nanoparticles by Neel and Brownian relaxations (hysteresis not included). For the mentioned frequency range (100 to 300 kHz), the optimal diameter in literature mostly falls within 12 and 20 nm (Deatsch, 2013). However, it is important to note that optimal radius also depends very heavily on the magnetic anisotropy and particle diameter, which will be further discussed.

Another important property that relates to the applied magnetic field frequency is the magnetic field geometry. The magnetic field geometry is defined as $\omega \tau$, where $\omega$ is the angular frequency of the applied magnetic field and $\tau$ is the effective relaxation time due to Neel and Brownian relaxation of the nanoparticle. When terms of magnetic field geometry falls in the $\omega \tau < 1$ window, the relaxation time is fast enough that thermal relaxation takes place within the timescale of a single magnetic field oscillation while when $\omega \tau > 1$, the magnetic field oscillates too fast for relaxation to occur (i.e. relaxation is blocked because the material is below the blocking temperature, $T_B$). SAR is at peak when $\omega \tau = 1$ as can be seen in the graph below:
Nanoparticle diameter

Magnetic nanoparticles generate thermal energy by three mechanisms: hysteresis loss, Brownian relaxation and Neel relaxation. The degree by which these mechanisms dominate depends mostly on the nanoparticle size. The critical size below which magnetite nanoparticles used in this thesis become superparamagnetic is somewhere in the range of 18-30 nm. Above this size, hysteresis loss appears significant while below it, hysteresis losses quickly become negligible as Neel and Brownian relaxations become more relevant. Below the critical size, Brownian relaxation becomes more dominant in larger particles while Neel relaxation is more significant in smaller particles. However, the division between Brownian and Neel relaxations becomes more dominant upon one another and depends strongly on the anisotropy constant of the particle.
Studies showed that the highest SAR will occur at a diameter just above the transition from superparamagnetism (Hergt, Validity limits of the Neel relaxation model of magnetic nanoparticles for hyperthermia, 2010) and (Bakoglidis, 2012). The reason is that at such point, both hysteresis effects and Neel relaxation effects may contribute. As the size increases, the extent by which Neel relaxation weakens and hysteresis effects become more significant depends on a number of parameters, including polydispersity, magnetic field magnitude, field frequency and anisotropy constant. Other factors such as particle concentration and aggregation/agglomeration also play a role; thus, it is difficult to have the two effects coincide for any single particle size in a given study. As a result, most studies report a maximum in SAR corresponding to a certain particle diameter; however, similar results may not be easily reproduced due to fine variations in samples that are difficult to replicate (polydispersity and aggregation/agglomeration).

*Nanoparticle anisotropy*

Every magnetic nanoparticle has some degree of anisotropy. The anisotropy is mainly due to inevitable asymmetry of particles which induces a preferred orientation for magnetic moment. Such orientation preference leads to an energy barrier which refers to the amount of energy that must be overcome in order to rotate the magnetic moment away from its preferred axis.

There are two sources of anisotropy; crystalline anisotropy and shape anisotropy. Crystalline anisotropy arises when a magnetic moment has a preferred direction of alignment along a crystalline axis. Shape anisotropy is a result of asymmetry in shape which leads to preferential alignment of atomic dipoles along the long axis of the non-spherical particle. The higher the anisotropy barrier in a particle, the more the
dominance of Brownian rotation over Neel relaxation. Therefore, in cubic or high aspect ratio particles, Brownian relaxation becomes highly dominant. Beyond the 20-nm range, heating by hysteresis loss may become significant. Hysteresis loss is affected significantly by anisotropy, since anisotropy contributes to the coercivity of a sample. As anisotropy increases, coercivity of the sample increases, hence hysteresis losses increase.

In all cases, studies showed that anisotropy is difficult to control and a measure which poses a major obstacle to the effective design of nanoparticles for optimizing hyperthermia applications. Magnetic anisotropy can be controlled to some degree by selecting the crystalline structure and shape of the nanoparticles. One way to control the shape of chemically precipitated iron oxide nanoparticles is by manipulating the particle growth rate. Gonzalez-Fernandez used ethanol to slow down the growth rate of nanoparticles producing cubic particles, while water alone produced spherical particles (Gonzalez-Fernandez, 2009). Due to their greater shape anisotropy, the cubic nanoparticles in these studies were shown to have higher SAR compared to spherical NPs. However, given the large size of these particles (45 nm), thermal energy was almost certainly generated by hysteresis losses, rather than Neel and Brownian relaxations.

Collective behavior

The high particle concentrations required for effective hyperthermia may result in strongly interacting systems, resulting in collective behavior of nanoparticles systems. While collective behaviors may appear as insignificant compared to other factors in the analysis, some studies showed their dramatic influence on SAR (Dennis, Nearly complete regression of tumors via collective behavior of magnetic nanoparticles in
hyperthemia, 2009). Generally, collective behavior arises from increasing particle concentration. Two independent phenomena are associated with collective behaviors; inter-particle spacing and aggregation. As particle concentration increases, inter-particle spacing decreases while particles may still maintain homogeneous distribution throughout the fluid. However, high-concentration nanoparticle solutions instead result in formation of aggregates. Therefore, inter-particle distances in a highly concentrated solution occur at two distinct scales; within aggregates and between aggregates and interactions at each scale influence SAR differently. Agglomeration occurs between these two extremes, in which nanoparticles are loosely bound within an inhomogeneous dispersion.

It is generally agreed that concentration-dependence arises due to the influence of inter-particle spacing on dipolar interactions. As concentration increases, the inter-particle distance decreases, thereby increasing dipolar interactions which alters the magnetic response of the ferrofluid. Most studies report a decrease in relaxation time as a result of increasing particle concentration. The effect of increased dipolar interactions and decreased relaxation time on SAR has long been a controversial subject. While no consensus has been reached, it can be generally deduced that the particle concentration-SAR relationship depends largely on the magnetic field geometry and particle size (Pineiro-Redondo, 2011).

When concentration increases, relaxation time decreases, so depending on whether the magnetic field geometry is in the $\omega \tau > 1$ or $\omega \tau < 1$ range, SAR will increase or decrease as concentration increases. If $\omega \tau < 1$, SAR decreases as concentration increases, while when $\omega \tau > 1$, SAR increases as concentration increases.
Aggregation was also seen to have an effect on SAR. As particles aggregate more, the magnetic field geometry tends to shift towards the $\omega \tau > 1$ thermally blocked regime, therefore, it can be generally inferred that for larger aggregated particles, SAR increases with increasing concentration and vice versa for smaller non-aggregated particles. However, it must be noted that even though aggregated particles exhibit a positive relationship between SAR and concentration, the SAR of non-aggregated particles at any given concentration is usually higher, meaning that ideal preparation of nanoparticles for heating should attempt to minimize aggregation as much as possible.

As for hysteresis, there have been very few studies conducted to examine the effect of particle concentration on hysteresis losses. (Eggeman, 2007), shows evidence of hysteresis above 5 kHz in aggregated samples and (Bakoglidis, 2012), shows nanoparticle heating attributable to hysteresis losses in 18-nm iron oxide nanoparticles. In the latter study, a high frequency of 765 kHz was used, which corresponds to a critical size of 10 nm beyond which hysteresis losses are expected to be dominant. However, particles as large as 13 nm in this study did not show significant heating attributable to hysteresis losses. This may suggest that the increase in particle concentration can delay the onset of hysteresis losses to a size greater than the theoretical critical size.

### 2.4 Theoretical and Experimental Power Loss Equations

The power loss corresponding to Neel or Brownian relaxation is approximately given by

$$ P = \frac{(mH_0\omega)^2}{2\tau k T p V(1+\omega^2\tau^2)} $$

(7)

taking (4) or (5) as relaxation time $\tau$; respectively. In Eq. (7), $m$ is the particle magnetic moment, $\omega$ the measurement angular frequency, $\rho$ the density of magnetite ($\rho = 5170$...
kg/m³) and \( H \) the field amplitude. \( P \) will reach maximum when \( \omega \tau = 1 \) after Debye [20]. Values of \( f = 100 \) kHz \( (\omega = 6.3 \times 10^5 \text{ s}^{-1}) \), \( k = 1 \times 10^{4} \text{J/m}^3 \) and \( T = 293 \text{K} \) lead to a calculated particle size of about 16.3 nm which makes \( \omega \tau = 1 \) and \( P_{\text{Neel}} \) reach a maximum. All samples used in this thesis were greater than this size; therefore, the heating losses are not attributed to Neel relaxation. Brownian relaxation was automatically not considered in this study since the NPs were immersed in viscous heavy oil that hinders the rotation of particles associated with Brownian relaxation.

Hysteresis was observed as the main heating mechanism for all tests in this thesis. One theory predicts that for large samples whose sizes exceed the domain wall width, domain wall motion causes magnetization reversal. As domain walls move through a sample, they become pinned at grain boundaries and additional energy is needed for them to continue moving. As a result, this pinning effect is one of the main sources of the coercivity, \( H_c \). For this case, theory predicts

\[
H_c = p_1 \frac{\sqrt{AK}}{J_s d} \propto d^{-1} \quad (8)
\]

where \( p_1 \) is a factor, \( A \) denotes the exchange stiffness, \( K \) is an effective anisotropy constant, \( J_s \) the exchange energy density and \( d \) the diameter of the particle. Therefore, reducing the grain size creates more pinning sites and increases \( H_c \). This theory is applicable for larger grain sizes. But for smaller particles, another theory applies as follows

\[
H_c = p_2 \frac{\kappa^4 d^6}{J_s A} \propto d^6 \quad (9)
\]
where $p_2$ is another factor. The dividing line between the two cases shown in Eqs. (2) and (3) is given by the ferromagnetic exchange length $d_{ex} = \sqrt{A/K}$. Since this thesis deals mostly with magnetite (Fe$_3$O$_4$) nanoparticles, the material parameters of magnetite ($K = 1.35 \times 10^4$ J/m$^3$, $A = 10^{-11}$ J/m) were used as reported by literature (Ming Ma, 2003) thus the exchange length is estimated to be $d_{ex} = 27$ nm. Below this size, $H_c$ will decrease rapidly as particle size decreases. Hysteresis loss can be approximated by computing the area of the hysteresis loop in an applied AC field. In the case of a nearly rectangular hysteresis loop, the hysteresis loss can be estimated by

$$P_{hys} = p_{hys} f M_s H_c$$

where $p_{hys}$ is a constant factor, $f$ the field frequency, $M_s$ the saturation magnetization and $H_c$ the coercivity. So, hysteresis loss of magnetite in AC magnetic field can be assumed to be proportional to coercivity, $H_c$ (Ming Ma, 2003). All tests performed in this thesis were above the size of $d_{ex} = 27$ nm, therefore Eq. (9) is an accurate model for predicting coercivity in this study. The general trend inferred from the equation is that when particle size decreases, coercivity increases. In this thesis, coercivity and magnetization saturation are measured by obtaining the hysteresis curve of the material. The method by which these are deduced from a hysteresis loop is described below:
As can be seen from the figure, in the case (a) where the hysteresis loop is plotted in terms of magnetization moment against applied magnetic field, the “intrinsic” coercivity, $H_{ci}$, is simply the $x$-intercept on the negative side. That is, intrinsic coercivity is defined as the reverse field that reduces the material’s magnetization to zero. The remanent magnetization, $M_r$, is the $y$-intercept since it is defined as the remaining magnetization in the material after the reverse field reduces to zero. The term “remanence” refers to the magnetic induction that corresponds to that remanent magnetization denoted by $B_r$. Both the actual coercivity, $H_c$, and remanence, $B_r$ can be easily calculated using the following equation:

$$B = \mu_0 (H + M)$$  \hspace{1cm} (11)
Where $M$ is the magnetization induced inside the sample by the applied magnetic field, $H$, and $\mu_0$ is the permeability of free space ($\mu_0=4\pi \times 10^{-7}$ m.kg/A$^2$.s$^2$) (Rudowicz). The hysteresis energy loss is then calculated using Eq. (10) which is then used to approximate Specific Loss Power (SLP). The specific loss power (SLP) describes the achievable power per gram of iron in the material. Theoretical SLP can be computed from the calculated hysteresis loss as follows:

$$SLP = \frac{P_{\text{phys}}}{m_{\text{NP}}}$$  \hspace{1cm} (12)

Where $m_{\text{NP}}$ is the mass of NPs used.

The computed SLP gives an estimation of the theoretically expected hysteresis losses which is compared to experimental Specific Absorption Rate (SAR). SAR is the general experimental method used to quantify SLP by measuring the amount of heat absorbed by the fluid for a given NP concentration. The equation used to calculate experimental SAR is given as follows:

$$SAR = C \frac{\Delta T}{\Delta t} \frac{1}{m_{\text{NP}}}$$  \hspace{1cm} (13)

where $C$ is the sample-specific heat capacity which is calculated as a mass weighted mean value of magnetite and bitumen. For magnetite, $C_{\text{mag}} = 0.937$ J/g K, and for water $C_{\text{wat}} = 4.18$ J/ g K, $\frac{\Delta T}{\Delta t}$ is the initial slope of the time dependent temperature curve. $m_{\text{Fe}}$ is the iron content per gram of the Fe$_3$O$_4$ suspension (Magnetic Nanparticle Heating).
Chapter 3: Nanoparticles Synthesis and Characterization

This chapter discusses the procedures used to prepare nanoparticles then the tests conducted to characterize their various properties.

3.1 Nanoparticles synthesis procedure

A total of 10 different types of magnetic nanoparticles were prepared for testing. Ferrite based nanoparticles have been reported in literature as hyperthermia agents. A number of researchers investigated the modulation of the magnetic heating by addition of metals or rare earth material to the ferrites. In this study, the effect of Co, Gd, Ce, Ho and Er on the hyperthermia characteristics of ferrites was investigated. The following table describes the acronyms used to refer to the nanoparticles in this thesis, its chemical composition and the ingredients of salts used to prepare these nanoparticles:
### Table 1: Preparation of MNPs

<table>
<thead>
<tr>
<th>Nanoparticle Acronym</th>
<th>Chemical Composition</th>
<th>Salts used for Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Fe$_3$O$_4$</td>
<td>100% Iron (III) Oxide (Fe$_3$O$_4$)</td>
<td>Iron(III) chloride hexahydrate (FeCl$_3$.6H$_2$O) (Sigma-Aldrich) and Iron(II) chloride tetrahydrate (FeCl$_2$.4H$_2$O) (Sigma-Aldrich)</td>
</tr>
<tr>
<td>2. Fe$_2$O$_3$</td>
<td>100% Iron (II) Oxide (Fe$_2$O$_3$)</td>
<td>Iron(III) chloride hexahydrate (FeCl$_3$.6H$_2$O) and Iron(II) chloride tetrahydrate (FeCl$_2$.4H$_2$O)</td>
</tr>
<tr>
<td>3. Fe/Er 75-25</td>
<td>75% Iron (III) Oxide (Fe$_3$O$_4$) and 25% Erbium (Er)</td>
<td>Iron(III) chloride hexahydrate (FeCl$_3$.6H$_2$O), Iron(II) chloride tetrahydrate (FeCl$_2$.4H$_2$O) and Erbium (III) Chloride anhydrous (ErCl$_3$)(Aldrich)</td>
</tr>
<tr>
<td>4. Fe/Ce 75-25</td>
<td>75% Iron (III) Oxide (Fe$_3$O$_4$) and 25% Cerium (Ce)</td>
<td>Iron(III) chloride hexahydrate (FeCl$_3$.6H$_2$O), Iron(II) chloride tetrahydrate (FeCl$_2$.4H$_2$O) and Cerium (III) Chloride Heptahydrate (CeCl$_3$.7H$_2$O) (Aldrich)</td>
</tr>
<tr>
<td>5. Co/Gd 75-25</td>
<td>75% Cobalt (II, III) Oxide (Co$_3$O$_4$) and 25% Gadolinium (Gd)</td>
<td>Cobalt (II) chloride (CoCl$_2$) (Aldrich) and Gadolinium (III) Chloride Hexahydrate (GdCl$_3$.6H$_2$O) (Aldrich)</td>
</tr>
<tr>
<td>6. Co/Ho 75-25</td>
<td>75% Cobalt (II, III) Oxide (Co$_3$O$_4$) and Holmium (Ho) 25%</td>
<td>Cobalt (II) chloride (CoCl$_2$) (Aldrich) and Holmium (III) Chloride Hexahydrate (HoCl$_3$.6H$_2$O) (Aldrich)</td>
</tr>
<tr>
<td>7. Co/Ce 75-25</td>
<td>75% Cobalt (II, III) Oxide (Co$_3$O$_4$) and Cerium (Ce) 25%</td>
<td>Cobalt (II) chloride (CoCl$_2$) (Aldrich) and Cerium (III) Chloride Heptahydrate (CeCl$_3$.7H$_2$O)(Aldrich)</td>
</tr>
<tr>
<td>8. Co/Er 75-25</td>
<td>75% Cobalt (II, III) Oxide (Co$_3$O$_4$) and Erbium (Er) 25%</td>
<td>Cobalt (II) chloride (CoCl$_2$) (Aldrich) and Erbium (III) Chloride anhydrous (ErCl$_3$) (Aldrich)</td>
</tr>
<tr>
<td>9. Fe/Ho 75-25</td>
<td>75% Iron (III) Oxide (Fe$_3$O$_4$) and 25% Holmium (Ho)</td>
<td>Iron(III) chloride hexahydrate (FeCl$_3$.6H$_2$O), Iron(II) chloride tetrahydrate (FeCl$_2$.4H$_2$O) and Holmium (III) Chloride Hexahydrate (HoCl$_3$.6H$_2$O) (Aldrich)</td>
</tr>
<tr>
<td>10. Fe/Gd 75-25</td>
<td>75% Iron (III) Oxide (Fe$_3$O$_4$) and 25% Gadolinium (Gd)</td>
<td>Iron(III) chloride hexahydrate (FeCl$_3$.6H$_2$O), Iron(II) chloride tetrahydrate (FeCl$_2$.4H$_2$O) and Gadolinium (III) Chloride Hexahydrate (GdCl$_3$.6H$_2$O)(Aldrich)</td>
</tr>
</tbody>
</table>
Even though the nanoparticles were made of different metal salts, the preparation method used for all samples was a chemical co-precipitation method. The principle used was the mixture of two salts that contain the magnetic element(s) then adding a reducing agent to oxidize the mixture in order to obtain the pure magnetic nanoparticles (MNP) precipitate. The procedure of preparing Fe$_3$O$_4$ NPs is presented below as an example to illustrate how this was accomplished:

1) In order to prepare Fe$_3$O$_4$, Iron(III) chloride hexahydrate (FeCl$_3$.6H$_2$O) and Iron(II) chloride tetrahydrate (FeCl$_2$.4H$_2$O) were mixed in a 3:2 ratio respectively. As a result, the masses of each salt required were calculated by stoichiometry as follows:

FeCl$_3$.6H$_2$O = 0.2g/L (Desired molarity) X 0.66 (Percentage of salt/solution) X 469.11g (Total mass of all salts added to solution) X 25ml (Volume of water) X 0.001L/g (Units conversion factor) = 1.5g.

FeCl$_2$.4H$_2$O = 0.2g/L X 0.34 X 469.11g X 25ml X 0.001L/g = 0.8g.

2) Therefore, 1.5 g of FeCl$_3$.6H$_2$O (yellow appearance) and 0.8 g of FeCl$_2$.4H$_2$O (green appearance) were weighed and added in a beaker containing 25ml of deionized water to produce an orange appearance solution.

3) The solution was heated while stirred with a magnetic stirrer for around 30 minutes until a temperature of 90°C was reached.

4) Next, the solution was sonicated for 10 minutes before the reducing agent was added. Then, 4ml of 8 Mol sodium hydroxide (NaOH) was pipetted until a black color appearance was seen and the solution was continued to be sonicated for
another 20 minutes. At this point, Fe$_3$O$_4$ has been produced in the solution and the next stage is to separate it from the solution by a washing process.

5) First, a magnet was used to attract the Fe$_3$O$_4$ particles towards the base of the beaker while leaving the solution at the upper layer. The solution was decanted until a wet precipitate of Fe$_3$O$_4$ remained in the beaker.

6) Deionized water was added onto the Fe$_3$O$_4$ precipitate and stirred to wash it from the solution. Then, the solution was centrifuged to allow the Fe$_3$O$_4$ particles to settle. The solution was decanted again and the process was repeated 4-5 times to make sure no other chemicals (other than water) were attached to the Fe$_3$O$_4$ precipitate.

7) The Fe$_3$O$_4$ precipitate was then heated in an oven at 60°C for 12 hours to make sure all the water evaporated.

8) After removing from the oven, Fe$_3$O$_4$ powder was placed in a test tube and crushed by a mortar to break solidified clusters and produce a fine powder of NPs.

A dry heating test that is more thoroughly described in Chapter 5 was first carried out. In the test, 500 mg of the dry MNP was electromagnetically heated by a magnetic coil, and the temperature rise over time was measured. The top two samples that generated the highest temperature rise were chosen as candidates for characterization. These were Fe/Er 75-25 and Fe$_3$O$_4$. It seemed that the addition of Erbium to Fe$_3$O$_4$ resulted in an improvement in heating, therefore, two more samples with different proportions of Erbium to Fe$_3$O$_4$ were prepared to further investigate the effect of Erbium percentage on heating efficiency. In total, these were the four types of samples that were characterized:

1. Fe$_3$O$_4$
2. Fe/Er 75-25: which consists of 75% $\text{Fe}_3\text{O}_4$ and 25% Erbium

3. Fe/Er 50-50: which consists of 50% $\text{Fe}_3\text{O}_4$ and 50% Erbium

4. Fe/Er 25-75: which consists of 25% $\text{Fe}_3\text{O}_4$ and 75% Erbium

Out of each mentioned nanoparticle types, different sizes of each sample were then prepared in order to study the effect of NP size on heating. In order to prepare different sizes of the same nanoparticle type, various preparation variables were controlled; the type and concentration of reducing agent used was changed and the temperature and time allowed for the reduction reaction was varied.

### 3.2 Particle Size

The particle size was measured by two different methods; the nanosizer and SEM imaging.

**Nanosizer**

ZetaSizer Nano-ZS was used to measure the average size of the NP samples prepared. A small quantity of the NP powder was dispersed in a cuvette containing water and placed into the device’s holder. When activated, the device transmits optical beams at a scattering angle of 90 degrees to measure particle size and molecule size. This technique measures the diffusion of particles moving under Brownian motion, and converts this to size and a size distribution using the Stokes-Einstein relationship was calculated. It was important to know that the device measures the bulk size of the particles in the sample and thus cannot distinguish between aggregated and non-aggregated particle. Therefore, it was important to crush the powder very well and sonicate it for 10 minutes prior to testing in order to minimize aggregation.
In this thesis, particle size is determined by two different tests, nanosizing and SEM images. The results of both tests for the same sample were compared to ensure accurate measurements. Below is an example of the report generated when running a sample with the Nanosizer test:

![Figure 6: Nanosizer sample report](image)

The result for this sample (Fe/Er 75-25) reveals that most of its particles (76%) have an average diameter of 118.5 nm while the rest (23.9%) have an average diameter of 470 nm. It is most likely that the big size particles of 470 nm existed as a result of aggregation since the sample was prepared using the same chemical process. Therefore, we assume the particles’ diameter to be 118.5 nm to eliminate aggregation measurement bias. All other nanosizer measurements are reported in a similar fashion. The sizes
revealed by nanosizer tests were next compared to sizes obtained from Scanning Electron Microscopy (SEM) images in order to confirm accuracy of measurements.

**Scanning Electron Microscopy (SEM)**

JEOL Model (JSM-6010Plus/A) was used to record images of a sample by scanning it with a focused beam of electrons. The NP powder was etched onto a gold plated stub and inserted into the SEM machine’s holder then the measurement process was initiated. The gold plating minimizes charge build up onto electrically insulated samples which helps improve the SEM image quality. The investigations were performed at 10-20 kV at a 10-15 times magnification range using an electro probe micro-analyzer. The digital micrographs were captured and stored on the computer.

The SEM images helped visualize the NPs aggregation level and confirmed the nanosizer’s size measurements. Below are the SEM images that were obtained:
The SEM images generally show aggregation taking place in most samples. Mostly for the Fe/Er 25-75 sample which is composed of the highest percentage of Erbium and...
lowest percentage of Fe₃O₄. Similarly, the least aggregation appears on the pure Fe₃O₄ NPs sample which suggests that increasing the percentage of Erbium added tends to increase aggregation in the sample. This observation may be explained by the tendency of Erbium NPs to aggregate given their high electrostatic charge density and their tendency to form atomic clusters (Sato, 2007). The JEOL 3D Image Software (MP – 45030TDI) was used to compute the average diameter of the particles in each sample which was compared to readings obtained from nanosizer readings. The results are shown below:

**Table 2: Nanosizer vs. SEM sizes**

<table>
<thead>
<tr>
<th>NP Sample</th>
<th>Nanosizer Diameter (nm)</th>
<th>SEM Diameter (nm)</th>
<th>Nanosizer Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄</td>
<td>40</td>
<td>37</td>
<td>92%</td>
</tr>
<tr>
<td>Fe/Er 75-25</td>
<td>100</td>
<td>91</td>
<td>90%</td>
</tr>
<tr>
<td>Fe/Er 50-50</td>
<td>87</td>
<td>80</td>
<td>91%</td>
</tr>
<tr>
<td>Fe/Er 25-75</td>
<td>99</td>
<td>100</td>
<td>99%</td>
</tr>
</tbody>
</table>

As can be seen in the table above, the nanosizer readings are shown to be above 90% accurate compared to SEM readings. To maintain consistency, the reported size for all samples tested in this thesis have been obtained from nanosizer measurements.

### 3.3 Chemical Composition

It was important to validate that the nanoparticle preparation techniques used resulted in the composition intended for. Therefore, the actual chemical composition was characterized using Energy Dispersive X-ray Spectroscopy (EDS).

**Energy Dispersive X-ray Spectroscopy (EDS)**

The same device (JEOL Model (JSM-6010Plus/A) that was used for SEM, had integrated EDS capability so that for each sample measured with SEM, EDS was run.
EDS is an analytical technique that emits a high energy X-ray beam to stimulate the sample and measure the X-ray peaks at which it excites. Its characterization capabilities are due to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its X-ray emission spectrum.

The EDS tests conducted were used to determine the actual chemical composition of the samples. Below is an example of the report produced for the Fe/Er 75-25 sample:

As can be seen, the EDS report revealed a makeup of 26.71% of Er and 73.29% Fe$_3$O$_4$ against an intended ratio of 25% and 75% respectively. This shows a close match between the prepared composition ratio and the actual one which confirms that the preparation techniques used were efficient. Below is the comparison between the intended compositions and the actual ones based on EDS results for tested samples:
Table 3: Planned vs. actual chemical composition

<table>
<thead>
<tr>
<th>No.</th>
<th>NP Type</th>
<th>Chemical Composition</th>
<th>NP Size (nm)</th>
<th>NP Conc. (g/ml)</th>
<th>Planne(d Fe3O4 %)</th>
<th>Actual Fe3O4 %</th>
<th>Comp. Accu.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bitumen only</td>
<td>NA</td>
<td>NA</td>
<td>0.00</td>
<td>0%</td>
<td>0%</td>
<td>100%</td>
</tr>
<tr>
<td>2</td>
<td>Fe/Er</td>
<td>75% Er and 25% Fe3O4</td>
<td>119</td>
<td>0.14</td>
<td>25%</td>
<td>31%</td>
<td>76%</td>
</tr>
<tr>
<td>3</td>
<td>Fe/Er</td>
<td>75% Er and 25% Fe3O4</td>
<td>119</td>
<td>0.30</td>
<td>25%</td>
<td>31%</td>
<td>76%</td>
</tr>
<tr>
<td>4</td>
<td>Fe/Er</td>
<td>75% Er and 25% Fe3O4</td>
<td>119</td>
<td>0.41</td>
<td>25%</td>
<td>31%</td>
<td>76%</td>
</tr>
<tr>
<td>5</td>
<td>Fe3O4</td>
<td>100% Fe3O4</td>
<td>40</td>
<td>0.18</td>
<td>0%</td>
<td>0%</td>
<td>100%</td>
</tr>
<tr>
<td>6</td>
<td>Fe3O4</td>
<td>100% Fe3O4</td>
<td>40</td>
<td>0.36</td>
<td>0%</td>
<td>0%</td>
<td>100%</td>
</tr>
<tr>
<td>7</td>
<td>Fe3O4</td>
<td>100% Fe3O4</td>
<td>40</td>
<td>0.54</td>
<td>0%</td>
<td>0%</td>
<td>100%</td>
</tr>
<tr>
<td>8</td>
<td>Fe/Er</td>
<td>50% Er and 50% Fe3O4</td>
<td>87</td>
<td>0.51</td>
<td>50%</td>
<td>46%</td>
<td>92%</td>
</tr>
<tr>
<td>9</td>
<td>Fe/Er</td>
<td>50% Er and 50% Fe3O4</td>
<td>70</td>
<td>0.34</td>
<td>50%</td>
<td>46%</td>
<td>92%</td>
</tr>
<tr>
<td>10</td>
<td>Fe/Er</td>
<td>50% Er and 50% Fe3O4</td>
<td>87</td>
<td>0.17</td>
<td>50%</td>
<td>46%</td>
<td>92%</td>
</tr>
<tr>
<td>11</td>
<td>Fe/Er</td>
<td>25% Er and 75% Fe3O4</td>
<td>100</td>
<td>0.51</td>
<td>75%</td>
<td>74%</td>
<td>99%</td>
</tr>
<tr>
<td>12</td>
<td>Fe/Er</td>
<td>25% Er and 75% Fe3O4</td>
<td>99</td>
<td>0.17</td>
<td>75%</td>
<td>74%</td>
<td>99%</td>
</tr>
<tr>
<td>13</td>
<td>Fe/Er</td>
<td>25% Er and 75% Fe3O4</td>
<td>100</td>
<td>0.34</td>
<td>75%</td>
<td>74%</td>
<td>99%</td>
</tr>
<tr>
<td>14</td>
<td>Fe/Er</td>
<td>75% Er and 25% Fe3O4</td>
<td>40</td>
<td>0.34</td>
<td>25%</td>
<td>31%</td>
<td>76%</td>
</tr>
<tr>
<td>15</td>
<td>Fe/Er</td>
<td>75% Er and 25% Fe3O4</td>
<td>90</td>
<td>0.34</td>
<td>25%</td>
<td>27%</td>
<td>92%</td>
</tr>
<tr>
<td>16</td>
<td>Fe/Er</td>
<td>50% Er and 50% Fe3O4</td>
<td>70</td>
<td>0.17</td>
<td>50%</td>
<td>50%</td>
<td>100%</td>
</tr>
<tr>
<td>17</td>
<td>Fe/Er</td>
<td>50% Er and 50% Fe3O4</td>
<td>70</td>
<td>0.50</td>
<td>50%</td>
<td>50%</td>
<td>100%</td>
</tr>
<tr>
<td>18</td>
<td>Fe/Er</td>
<td>75% Er and 25% Fe3O4</td>
<td>106</td>
<td>0.34</td>
<td>25%</td>
<td>25%</td>
<td>100%</td>
</tr>
</tbody>
</table>

As can be seen in the table, the actual composition was 76% to 100% accurate compared to the planned composition during preparation of the NPs. Nevertheless, all analysis in this thesis is based on actual compositions to maintain the highest degree of reliability during correlations.
3.4 Morphology

Morphology refers to the degree of crystallinity in the samples and was measured for the samples using XRD.

*X-ray Diffraction (XRD)*

X-ray diffraction analysis was performed using XRD 6100, Shimadzu, in order to evaluate the crystalinity of the sample. An aluminum sample holder was filled with the powder sample and was pressed properly with wax paper to prevent any voids. The diffraction patterns of the powders were recorded using Cu Kα radiation. The scan range was from 20 to 80 with step 2θ=0.02 with scan speed of 2 degree/minute. The characteristic x-ray diffraction pattern generated in a typical XRD analysis provides a unique “fingerprint” of the crystals present in the sample. When properly interpreted, by comparison with standard reference patterns and measurements, this fingerprint allows identification of the crystalline form.

The four samples were tested for XRD where each sample was labeled as follows:

*Table 4: XRD samples*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>75% Fe$_3$O$_4$ and 25% Er</td>
</tr>
<tr>
<td>B</td>
<td>50% Fe$_3$O$_4$ and 50% Er</td>
</tr>
<tr>
<td>C</td>
<td>25% Fe$_3$O$_4$ and 75% Er</td>
</tr>
<tr>
<td>D</td>
<td>100% Fe$_3$O$_4$</td>
</tr>
</tbody>
</table>
The expected peaks for Fe$_3$O$_4$ and Er are shown below:

Table 5: Er XRD peaks

<table>
<thead>
<tr>
<th>2θ</th>
<th>Crystal Plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.31</td>
<td>(101)</td>
</tr>
<tr>
<td>51.67</td>
<td>(110)</td>
</tr>
<tr>
<td>57.81</td>
<td>(103)</td>
</tr>
<tr>
<td>61.99</td>
<td>(112)</td>
</tr>
</tbody>
</table>

Table 6: Fe$_3$O$_4$ XRD peaks

<table>
<thead>
<tr>
<th>2θ</th>
<th>Crystal Plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.19</td>
<td>(220)</td>
</tr>
<tr>
<td>35.56</td>
<td>(311)</td>
</tr>
<tr>
<td>43.25</td>
<td>(400)</td>
</tr>
<tr>
<td>57.19</td>
<td>(511)</td>
</tr>
<tr>
<td>62.81</td>
<td>(440)</td>
</tr>
</tbody>
</table>

The XRD results for all four samples are shown in the graph below. The dotted grey lines represent the peaks for Fe$_3$O$_4$ while the orange lines represent the peaks for Er.
As can be seen in Figure 9, the peaks for Fe₃O₄ are clearly evident and exist at a high CPS (Sample A). The samples containing Er have less CPS and the Fe₃O₄ peaks in the Fe/Er samples attenuate more as the percentage of Fe₃O₄ decreases. The peaks for Er in all three samples are hardly visible. It can be inferred that the Fe₃O₄ sample is highly crystalline while crystallinity of the Fe/Er samples reduce as the percentage of Er increases due to its non-crystalline morphology in the compound. In relation to the aggregation noticed from SEM images, it can be inferred that as the percentage of Er increases, the particles tend to aggregate and the sample loses its crystallinity.
3.5  Coercivity

Coercivity of one sample (Fe/Er 75-25 which consists of 75% $\text{Fe}_3\text{O}_4$ and 25% Er) was measured in order to correlate the coercivity obtained from the sample to the heating obtained experimentally.

*Superconducting Quantum Interference Device (SQUID)*

A SQUID test was carried out by an external vendor and was to measure the hysteresis loop for Fe/Er 75-25. A SQUID is a highly sensitive magnetometer used to measure very small magnetic fields, based on superconducting loops generated in the material. The magnetometer measures the magnetization of a small sample of magnetic material placed in an external magnetizing field by converting the dipole field of the sample into an AC electrical signal. This is performed separately over a wide range of temperatures in order to understand the effect of temperature. By measuring the field of an external electromagnet, it is possible to obtain the hysteresis curve of a material.

The Fe/Er 75-25 sample was tested with a SQUID and the following hysteresis curve was generated for the temperature range covered:
As can be seen in Figure 10, the curve shows that as the temperature decreases, the magnetization moment increases for the same magnetic field. It was also observed upon closer look at the curves that the coercivity also increased as temperature decreased. This behavior suggests that the tested temperature range is below the blocking temperature (TB) of the Fe/Er 75-25 sample. i.e.: the blocking temperature is greater than 300 K (27°C), which means that the particle tested is not of superparamagnetic nature. This agrees with theory since the size of this nanoparticle (119nm) is above the critical size of 27 nm. The enhanced magnetization and coercivity at lower temperatures has been attributed to an increase in anisotropy barrier as temperature decreases which increases the effects of thermal fluctuations of the blocked moment.

It can also be noticed that, below 50 K, an abrupt increase in magnetization of nanoparticles was observed. This increase in magnetization at 5K was explained with
reference to the presence of frozen surface-spins and some paramagnetic impurities (Erbium) at the shell of nanoparticles that are activated at lower temperatures in the Fe/Er nanoparticles (Maaz, 2010).

The next figure (Figure 11) shows the hysteresis curve for the sample at room temperature 300 K (27°C) only.

![Fe/Er 75-25 Hysterisis Curve at 300K](image)

*Figure 11: Hysteresis curve for Fe/Er 75-25 at 300 K only*

It can be noticed that the moment does not seem to saturate at the maximum magnetic field applied by the SQUID (3000 Oe) which suggests that the susceptibility of this material can be further increased if tested over a wider range of magnetic field. However, for the purpose of this thesis, the saturation magnetization cannot be inferred due to this reason which means the hysteresis power loss cannot be calculated (area under the positive curve).
The curve is essentially two curves consisting of forward field and reverse field which cannot be distinguished at this scale. The forward field curve refers to the response when the applied magnetic field was first increased from -3000 Oe to 3000 Oe while the reverse field curve is the response when the field was then reduced from 3000 to -3000 Oe. The reverse field curve is always higher than or overlaying the forward field curve since magnetic materials tend to possess a remanent magnetization characteristic. In order to see the separation of the two curves and calculate the coercivity, a close up image of the curve was taken as shown below:

![Fe/Er 75-25 Hysteresis Loop at 300 K](image)

*Figure 12: Hysteresis loop Fe/Er 75-25 (coercivity and remanence)*

As can be seen in Figure 12, the intrinsic coercivity of this sample is observed at the x-intercept of the reverse field curve at 68 Oe. The hysteresis power loss cannot be calculated since the saturation magnetization cannot be deduced from the test. It is
advised for future work that the sample is tested beyond a magnetic field of 3000 Oe until saturation magnetization is reached (slope of curve approaches zero).
Chapter 4: Electromagnetic Heating Experiments

This chapter describes the experimental setup and procedure for electromagnetically heating different nanoparticle samples in different fluid mediums. The samples are initially heated in a dry state, then in a water medium and finally thorough testing conducted in bitumen mixtures. A typical temperature-viscosity relationship of heavy oil is presented in order to clarify the effect of temperature increase on viscosity. A magnetic coil is used to generate heat and the heating is measured by temperature rise and SAR is calculated accordingly.

4.1 Bitumen’s Viscosity vs. Temperature

The major objective of this thesis is to maximize the EM heating output in bitumen samples so that their viscosity decreases and they can be easily pumped up from reservoirs. Therefore, it is important to know how viscosity relates to temperature.

The following graph shows the viscosity of naturally existing bitumen at virgin reservoirs and the relationship of temperature with viscosity (ExxonMobil).
As can be seen, bitumen naturally exists at above 1,000,000 cP and when heated, the viscosity almost linearly decreases with temperature until 100°C after which the viscosity decreases with temperature at a slower rate. The current Steam Assisted Gravity Drainage (SAGD) process heats up the bitumen to a temperature of almost 200°C at which the viscosity is almost 10cP. In this study, however, the temperature could not be raised above 80°C due to experimental limitations. However, for the sake of simplification, it can be concluded that for any rise in temperature achieved in our experiments a linear reduction in viscosity occurred.
4.2 Electromagnetic Heating Setup

Coil setup

The schematic below illustrates the coil setup used to heat up the samples tested:

![Coil setup schematic](image)

*Figure 14: Coil setup schematic*

The function of the coil is to generate a magnetic field that stimulates the nanoparticles in the sample, thus generating heat. The EM heating setup consisted of three main sub-systems: a coil, cooling system, power and circuit components; all purchased from RMC Cybernetics and assembled in house. The coil had a diameter of 41mm and was made of four turns of hollow copper pipe to allow for water circulation for cooling purposes. A parallel set of 8 heavy duty capacitors were welded onto the coil each rated at 330nF for a maximum of 400V. The capacitors allowed the coil to have a fairly high resonant frequency at 107 kHz which is ideal for heating small objects. A pump was used to circulate water into the coil continuously to cool it down and make sure that any heat generated in the test sample is solely due to electromagnetic excitation rather than Ohmic heat losses generated in the coil and transferred to the sample by conduction and convection.
A high voltage DC power supply powered the collector resonance oscillator circuit which was in turn connected to the center tap of the coil. The oscillator circuit had two main functions; to convert the DC input into an AC current supplied to the coil which is required for EM wave generation and the most important function is that it automatically supplied the current at the resonant frequency of the coil. Working at resonant frequency meant that the coil operated at maximum power efficiency with minimal losses. A Power Pulse-width Modulator (PWM) was also connected to the circuit to allow controlling the duty cycle (pulse width) and switching frequency separately from the DC power supply controls. This ensured safe operation of the circuit to prevent overloading of the coil components by limiting the duty cycle to 80% of the power from the DC supply. An oscilloscope was used to measure the frequency of the AC signal supplied, the peak-to peak and RMS voltages, while an ammeter was connected to measure the current draw. The below images illustrate the coil setup and components described:
Figure 16: Resonance oscillator

Figure 17: Top view of sample in coil and capacitors connected in parallel
Figure 18: Sample inserted in coil (front view)

Figure 19: Water circulation connections
Figure 20: The Power Pulse Width Modulator (PWM)

Figure 21: Ammeter measuring current draw
General heating procedure

A standard procedure was followed to prepare a sample of nanoparticle dispersed in a base fluid (the mixture is called nanofluid). A sample was prepared by mixing a 5 ml volume of fluid with a weighted mass of nanoparticle then mixing them in a 10 ml PVC test tube using a stirrer. Once a sample was prepared, a digital thermocouple was used to measure the sample’s initial temperature. The test tube was then immersed into the coil at its center to ensure even heating and the DC power supply was switched on to start EM wave generation inside the coil. Temperature readings were taken at 10 minute intervals by removing the tube from the coil and using the thermocouple to record a reading. The sample was then immersed again to continue heating. Removing the sample from the coil ensured that the readings taken were not affected by the EM heating of the thermocouple metal tip when exposed to EM waves, thus making sure that the temperature reading is a result of the sample being heated up by EM heating phenomenon. Each test was performed for a total period of 60 minutes so a total of 6 temperature readings were taken per test.

4.3 Heating of Dry NPs

At first, the 10 different types of NPs were heated in their dry states alone in order to determine the ones that generated the most heat and were used as candidates for further testing. NPs were prepared in a dry powder and 500mg of each NP type were placed in a plastic test tube. Then, heating tests were performed for each sample separately by placing the test tube inside the coil and measuring the sample temperature at 10 minute intervals. The objective was to determine the maximum increase in temperature for each NP type which is shown in the chart below (Figure 22):
As can be seen in Figure 22, Fe/Er 75-25 NPs generated the greatest rise in temperature followed by Fe$_3$O$_4$. Therefore, Fe/Er and Fe$_3$O$_4$ were further characterized and tested with other fluids in order to better understand the factors influencing their heating output.

### 4.4 Heating of Water Dispersed NPs

In this series of tests, the objective was to observe the maximum temperature rise when Fe/Er 75-25 and Fe$_3$O$_4$ NPs are immersed in water compared to their dry state and to roughly test the effect of NP concentration in water on temperature rise. A sample containing 1 ml of water only was used as a control to deduce the incremental temperature rise generated by presence of NPs in the sample.
Figure 23 reveals that the temperature rise for the same mass of dry NPs immersed in 1 ml water generates a smaller temperature rise when compared to their dry state. For example, 500 mg of Fe$_3$O$_4$ generated a 17.9°C temperature rise in its dry state but only 13°C when dispersed in 1 ml of water. Fe/Er, however, generated 23°C when dry and 19°C in 1 ml of water. This is explained by the energy transfer process that occurs. MNPs are first excited by the magnetic field and generate heat through hysteresis or relaxation losses. The heat generated is identified as the heat source. Part of this heat is stored in the material causing its temperature to rise based on its specific heat capacity and the other part is lost to the surroundings by conduction and convection currents. When in their dry state, the MNPs only lose heat to air while when dispersed in water. The heat is first conducted and stored in the water causing its temperature to rise. The heat is then lost to the surrounding air by conduction and convection. Due to the lower thermal conductivity of air and since some energy is stored by the water, the temperature rise for MNPs dispersed in water is less than when they are in their dry state.
Another observation in Figure 23 is that when the concentration of Fe₃O₄ NPs in water was increased, the temperature rise increased. This is explained by the increase in mass of NPs for the same volume of water, allowing a greater amount of magnetic energy to be absorbed and converted into heat, thus generating a greater rise in temperature.

4.5 Heating of Bitumen Dispersed NPs

The next series of tests involved dispersing the NPs in bitumen in order to simulate the heating generation process for the application of heavy oil. The general theme was preparing the dry NPs in powder form, mixing them in a volume of bitumen and then heating the sample in the coil for a 90 minute test period while taking temperature readings at 10 minute intervals.

The volume of bitumen fluid and mass of NPs used was varied between the same NP type and size in order to study the effect of NP concentration (mass of NP per unit volume of bitumen) on heating. However, for comparing the effect of NP size of the same NP type on heating, the concentration needed to be maintained equal for the two samples as a control. It must be noted, however, that it was difficult to maintain the same volume of bitumen for such samples due to the high viscosity of bitumen as it was being poured. Therefore, when concentration was attempted to be set, a volume of bitumen was poured and measured, then the proportion of mass of NPs required to achieve the concentration required was added. Therefore, the normalization scheme used to compare the preparation of different samples was NP concentration (mass of NPs per unit volume of bitumen).

Below is a complete list of all tests performed in bitumen with different sizes of NPs and different nanoparticle alloy compositions.
Table 7: NPs in bitumen experiments

<table>
<thead>
<tr>
<th>No.</th>
<th>NP Type</th>
<th>Chemical Composition</th>
<th>NP Size (nm)</th>
<th>Mass of NPs (g)</th>
<th>Volume of Bitumen (ml)</th>
<th>NP Concentration (g/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bitumen only</td>
<td>NA</td>
<td>NA</td>
<td>0.00</td>
<td>1.0</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>Fe/Er</td>
<td>75% Er and 25% Fe3O4</td>
<td>119</td>
<td>0.50</td>
<td>3.6</td>
<td>0.14</td>
</tr>
<tr>
<td>3</td>
<td>Fe/Er</td>
<td>75% Er and 25% Fe3O4</td>
<td>119</td>
<td>0.83</td>
<td>2.8</td>
<td>0.30</td>
</tr>
<tr>
<td>4</td>
<td>Fe/Er</td>
<td>75% Er and 25% Fe3O4</td>
<td>119</td>
<td>1.12</td>
<td>2.7</td>
<td>0.41</td>
</tr>
<tr>
<td>5</td>
<td>Fe3O4</td>
<td>100% Fe3O4</td>
<td>40</td>
<td>0.45</td>
<td>2.5</td>
<td>0.18</td>
</tr>
<tr>
<td>6</td>
<td>Fe3O4</td>
<td>100% Fe3O4</td>
<td>40</td>
<td>1.08</td>
<td>3.0</td>
<td>0.36</td>
</tr>
<tr>
<td>7</td>
<td>Fe3O4</td>
<td>100% Fe3O4</td>
<td>40</td>
<td>1.62</td>
<td>3.0</td>
<td>0.54</td>
</tr>
<tr>
<td>8</td>
<td>Fe/Er</td>
<td>50% Er and 50% Fe3O4</td>
<td>87</td>
<td>1.02</td>
<td>2.0</td>
<td>0.51</td>
</tr>
<tr>
<td>9</td>
<td>Fe/Er</td>
<td>50% Er and 50% Fe3O4</td>
<td>70</td>
<td>1.02</td>
<td>3.0</td>
<td>0.34</td>
</tr>
<tr>
<td>10</td>
<td>Fe/Er</td>
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<td>0.34</td>
<td>2.0</td>
<td>0.17</td>
</tr>
<tr>
<td>11</td>
<td>Fe/Er</td>
<td>25% Er and 75% Fe3O4</td>
<td>100</td>
<td>1.02</td>
<td>2.0</td>
<td>0.51</td>
</tr>
<tr>
<td>12</td>
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<td>2.0</td>
<td>0.17</td>
</tr>
<tr>
<td>13</td>
<td>Fe/Er</td>
<td>25% Er and 75% Fe3O4</td>
<td>100</td>
<td>1.02</td>
<td>3.0</td>
<td>0.34</td>
</tr>
<tr>
<td>14</td>
<td>Fe/Er</td>
<td>75% Er and 25% Fe3O4</td>
<td>40</td>
<td>1.02</td>
<td>3.0</td>
<td>0.34</td>
</tr>
<tr>
<td>15</td>
<td>Fe/Er</td>
<td>75% Er and 25% Fe3O4</td>
<td>90</td>
<td>1.02</td>
<td>3.0</td>
<td>0.34</td>
</tr>
<tr>
<td>16</td>
<td>Fe/Er</td>
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<td>70</td>
<td>0.33</td>
<td>2.0</td>
<td>0.17</td>
</tr>
<tr>
<td>17</td>
<td>Fe/Er</td>
<td>50% Er and 50% Fe3O4</td>
<td>70</td>
<td>1.00</td>
<td>2.0</td>
<td>0.50</td>
</tr>
<tr>
<td>18</td>
<td>Fe/Er</td>
<td>75% Er and 25% Fe3O4</td>
<td>106</td>
<td>0.85</td>
<td>2.5</td>
<td>0.34</td>
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</table>

To illustrate the general profile exhibited by all bitumen heating tests, Figure 24 shows the temperature vs. time profile for two of the tests performed for Fe/Er 75-25, Fe/Er 50-50, Fe/Er 25-75 and pure Fe3O4 NP samples.
The concentrations of the samples were maintained relatively constant in order to make fair comparisons; however, there were slight variations (0.14g/ml to 0.18g/ml) due to difficulties during sample preparation which are assumed to have a negligible effect on the results. The graph shows that there is a rapid increase in temperature initially in the first 10 minutes which then starts to gradually slow down and eventually stabilizes at around the 60 minute mark. The same trend was demonstrated by all the tests performed. The slope of temperature rise in the first 10 minutes is related to the magnetic susceptibility of the MNPs. The higher the magnetic susceptibility of the MNP, the more heat they generate allowing the samples to reach higher temperatures. As can be seen, Fe/Er 75-25 reaches the highest temperature among all other samples which may be explained by its higher magnetic susceptibility. The reason why the temperature stabilizes is owed to the Curie-Dwelling temperature phenomenon. MNPs generate heat until they reach a temperature known as their Curie temperature. Beyond that point, the
MNPs no longer react magnetically to the changing magnetic field, thus no heat is generated causing the temperature to stabilize at the Curie temperature ($T_c$). However, when dispersed in a fluid, a portion of the energy absorbed is lost to the surrounding fluid by conduction and convection. Therefore, the ferrofluid’s temperature stabilizes at a temperature below the MNP’s Curie temperature which is known as the dwell temperature (Zhang, 2008). In literature, most ferrite nanoparticles of the nanoparticle size ranges tested in this study (40-118nm) are reported to have a Curie temperature between 30°C and 60°C (Kuznetsov, ESR study of thermal demagnetization processes in ferromagnetic nanoparticles with Curie temperature between 40 and 60C, 2006, 2006). This agrees with the results seen in the graph as the dwell temperature for Fe/Er 75-25 was around 41°C. For Fe/Er 50-50, it was 39°C, for Fe/Er 25-75 it was around 37°C, and for Fe$_3$O$_4$ it was around 35°C. The SQUID result for Fe/Er 75-25 revealed that the blocking temperature is above 27°C which indicates that it has a Curie temperature above 27°C and agrees with the dwell temperature seen at 41°C. The graph clearly shows that the addition of 25% of Erbium to Fe$_3$O$_4$ resulted in a 6°C increase in the dwell temperature (17% increase) and that for every 25% added beyond the 25% weight ratio of Erbium, a 2°C reduction in dwell temperature occurred. It may thus be inferred that the optimal percentage of Erbium lies in the vicinity of 25%.

Using the initial slope of the temperature-time curve shown above and concentration of NPs in bitumen used for each test, SAR is calculated. SAR is the general experimental method used to quantify the amount of heat absorbed by the fluid for a given NP concentration which ensures that heating results are not biased by mass of NPs nor volume of fluid used. This allows making comparison of effects of other factors such as
NP concentration, NP size and chemical composition. The equation used to calculate experimental SAR is given as follows:

\[
SAR = C \frac{\Delta T}{\Delta t} \frac{1}{m_{NP}}
\]  

where \( C \) is the sample-specific heat capacity which is calculated as a mass weighted mean value of magnetite and bitumen. For magnetite, \( C_{mag} = 0.937 \text{ J/g K} \), and for water \( C_{wat} = 4.18 \text{ J/g K} \), \( \frac{\Delta T}{\Delta t} \) is the initial slope of the time dependent temperature curve. \( m_{NP} \) is the iron content per gram of the \( \text{Fe}_3\text{O}_4 \) suspension. The effect of nanoparticle size, concentration and chemical composition on SAR is presented in the next section.
Chapter 5: Results and Discussion

This chapter presents the effect of varying NPs in bitumen concentration (mass of NPs per unit volume of bitumen), NP size, and chemical composition on the temperature rise and SAR.

5.1 Effect of Concentration

The linear least squares fitting technique was used with the experimental data points to obtain a regression that correlates between NPs concentration and temperature rise. As can be seen in Figure 25, for all samples the temperature of the bitumen solution increases in a linear fashion as the concentration of NPs increases. This is explained as follows: when the ratio of mass of MNPs to bitumen increases, the effective heat capacity of the sample decreases since ferrite NPs have a lower specific heat capacity.
than the bitumen (0.937 J/g°C for Fe₃O₄ NPs and 2.093 J/g°C for bitumen). This means that as NP concentration increases, it takes less heat energy to raise the temperature of the sample by 1°C and since the heat emitted by the coil is constant (due to fixed power input), this translates into a larger temperature rise for samples that have higher concentrations of NPs in bitumen.

All curves have a y-intercept of around 2.8°C which represents the temperature rise of the bitumen sample when no NPs are mixed in it. The reason bitumen heats up in a magnetic coil, even without having MNPs in it, is the presence of ionic compounds in the composition of the bitumen that are stimulated by the magnetic field. In order to estimate the contribution of temperature rise due to adding NPs, 2.8°C is subtracted from the total temperature rise.

It can be noticed that the particles tested were of different sizes as it was difficult to control particle size during preparation. Equation 8 predicts that the smaller the particle size, the greater the hysteresis heating. Therefore, keeping this concept in mind, a comparison of heating effectiveness between the different types of NPs is made. The graph in Figure 25 reveals that even with the biggest particle size among the other samples, the Fe/Er 75-25 sample (116nm) is able to generate the most heat in the solution which suggests an enhanced heating ability of Fe₃O₄ as a result of adding a 25% Er additive. As the percentage of Erbium added increased, the temperature rise decreased which suggests that the optimal percentage of Erbium lies somewhere around the 25% range but lower than 50% (since the temperature rise for 50% Er was lower than 25% Er). XRD and SEM characterization has revealed a decrease in crystallinity and an increase in aggregation level as the percentage of Erbium added to Fe₃O₄ was increased. Therefore, it may be the case that even though Erbium may have magnetic
properties that are superior to Fe$_3$O$_4$ due to which its addition to Fe$_3$O$_4$ increases the temperature rise, the excessive addition of Erbium causes loss of crystallinity and a tendency to aggregate which hinders the magnetic susceptibility of the particles as reported in literature.

The coefficient of determination of the fitted lines (R2 values) were used to understand the strength of the linear correlation formed from the experimental results. R2 values for all lines fitted are above 0.9 indicating a strong linear relationship between concentration and temperature rise except for the Fe/Er 50-50 (87 nm) sample which exhibits a weak linear relationship of temperature with concentration given an R2 of only 0.51 (which can be explained by experimental errors).

The increase in temperature per concentration of NPs in the bitumen dispersion is examined by calculating SAR values as seen in the following graph.
Figure 26: NPs in Bitumen Concentration vs. SAR

Figure 26 shows that for all particle types except Fe/Er 75-25, the SAR decreases slightly as the concentration of the NP increases in bitumen. This is explained by the collective behavior where two factors affect the SAR-concentration relationship; magnetic field geometry and level of aggregation. As the concentration increases, interparticle spacing decreases and dipolar interaction increases causing either an increase of SAR when magnetic field geometry lies in the unblocked ($\omega \tau < 1$) and a decrease in SAR when it lies in the blocked ($\omega \tau > 1$) regime. On the other hand, when concentration increases, aggregation is more likely to occur which may hinder effective magnetic field absorption by the nanoparticles, hence reducing the SAR.

In order to understand whether each sample was positioned in the blocked or unblocked regime while being tested, the blocking temperature of each sample needs to be
understood which can be estimated by the Curie temperature revealed in the experiments. It was found in the previous chapter that the Curie temperatures of the samples can be roughly estimated as follows: 35°C for pure Fe$_3$O$_4$, 37°C for Fe/Er 25-75, 39°C for Fe/Er 50-50, and 41°C for Fe/Er 75-25. Therefore, it can be seen that the addition of Erbium increased the Curie temperature of Fe$_3$O$_4$ in such a way that the Fe$_3$O$_4$ compound in any Fe/Er mixture was pushed further ahead of its original blocking temperature of 35°C. Assuming so means that all Fe/Er samples fall above the blocking temperature of Fe$_3$O$_4$, hence they all lay in the unblocked regime of $\omega\tau<1$ and any increase in concentration is expected to result in an increase in SAR. However, as the concentration increases, aggregation increases which adversely affects SAR. The case of Fe$_3$O$_4$ is simple since the regime is clearly blocked (temperature is less than its blocking temperature and $\omega\tau>1$). Hence, it easily follows theory that as the concentration increases, the SAR decreases. In the case of Fe/Er 75-25, the Curie temperature was 6°C ahead of Fe$_3$O$_4$’s blocking temperature of 35°C; therefore, a strong increase of SAR as a result of increasing concentration was achieved. This strong increase in SAR offset the effect of aggregation given that Fe/Er 75-25 had the least aggregation and hence resulted in an overall increase in SAR as the concentration increased. However, the other two samples, Fe/Er 50-50 and Fe/Er 25-75, were further behind Fe$_3$O$_4$’s blocking temperature (4°C and 2°C respectively) and they also contained a lower percentage of Fe$_3$O$_4$, hence the effect of Fe$_3$O$_4$ on the sample due to it being ahead of its blocking temperature was minimal. These samples also revealed a higher level of aggregation in SEM images. This means that the slight increase of SAR as concentration increased due to being in the unblocked regime ($\omega\tau<1$) was not enough to offset the effect of
aggregation on decreasing SAR, hence an overall decrease in SAR was achieved as concentration increased.

5.2 Effect of NP Size

The graph (Figure 27) shows the effect of varying particle size for Fe/Er 50-50 samples. As the particle size was reduced from 87nm to 70nm, there was an almost two times increase in SAR. This agrees with the literature review presented earlier in the sense that the particles are larger than the exchange length computed in the literature estimated to be $d_{ex} = 27$ nm, below which Equation 8 applies:

$$H_c = \frac{\sqrt{\lambda \kappa}}{\mu_d^2} \propto d^{-1}$$  \hspace{1cm} (8)
Where $H_c$ is the coercivity, $p$ is a factor, $A$ denotes the exchange stiffness, $K$ is an effective anisotropy constant, $J_s$ is the exchange energy density and $d$ is the diameter of the particle. The equation implies coercivity, hence hysteresis loss increases as particle size decreases ($H_c \propto d^{-1}$). In this case, a 20% decrease in size (from 87nm to 70nm) resulted in a 100% increase of SAR (from 0.13 to 0.26).

Since the sample Fe/Er 75-25 showed the most significant heating ability, the effect of NP size on temperature rise and SAR was investigated for this MNP type as seen in Figure 28.

![Figure 28: Fe/Er 75-25 NP Size vs. Temperature](image)

The graph shows a tendency for temperature rise to decrease as the size of NP increases. Since, it is not subjective to make comparisons between the amounts of heat generated without normalizing the temperature rise to the concentration of NP used per unit volume of bitumen used, the SAR values were computed as seen below in Figure 29.
A strong linear relationship with a high $R^2$ of 0.93 is seen to exist between SAR and NP Size. As the NP Size increases, the SAR decreases. All particles exceeded the exchange length computed of $d_{ex}=27$nm such that the theoretical model implies that hysteresis loss in that case is expected to be inversely proportional to diameter (Equation 8):

$$H_c = p_1 \frac{\sqrt{AK}}{Jsd} \propto d^{-1}$$

(8)

The experimental results shown in the graph confirm this trend. The slope of the fitting line is -0.0017 which implies that for every increase in 10nm size, the SAR decreases by 0.017. The reduction of size from 119nm to 33nm (72% reduction) resulted in an 88% increase in SAR (from 0.17 to 0.32).
5.3 Effect of Chemical Composition

The Fe/Er samples of various ratios of Fe3O4 to Er were analyzed to see the effect of Er % on the temperature and SAR. Note that the actual Er percentages measured by EDS were used for analysis rather than planned Er %.

As can be seen in Figure 30, the general trend is that as the percentage of Er increases in the Fe/Er sample, the temperature rise decreases. The R² values of all linearly fitted lines are above 0.9 which suggests a strong linear relationship between Er% and temperature rise. That is not to say that an Er-free sample (100% Fe₃O₄) would generate the highest temperature rise since it has already been shown in previous results that the addition of 25% of Er in an Fe₃O₄ sample increases its heating ability greatly.

Figure 30: Fe/Er effect of Er % on temperature
The graph also shows that the maximum temperature rise occurred at the medium level concentration (0.34g/ml) while the lowest temperature rise occurred at the lowest concentration (0.17g/ml). That is explained by the increased effective susceptibility and reduced effective specific heat capacity upon addition of magnetic nanoparticles in the bitumen fluid. However, in order to understand the normalized effect, SAR values were computed as shown in Figure 31.

![Fe/Er Actual Er % vs. SAR](image)

*Figure 31: Fe/Er effect of Er % on SAR*

Again, the SAR generally decreased with increasing Er percentages suggesting that the optimal Er percentage for maximum heating lies somewhere between 0% and 25% as
best SAR values were obtained in this study at a 25% Er followed by 50% Er then 0% Er (pure Fe3O4) and finally 75% Er.

In terms of concentration, the optimal concentration was observed to occur at 0.34g/ml while the maximum and minimum concentrations of 0.17g/ml and 0.51g/ml seemed to show similar SAR levels. This can be explained by the collective behavior concept such that the initial increase from 0.17g/ml to 0.34g/ml caused dipolar interactions to increase, hence decreasing relaxation times and increasing SAR. However, when concentration increased from 0.34g/ml, the particles tended to form aggregates that obstructed efficient heat transfer, thus reduced SAR.

The reason behind the enhanced heating performance by adding only a small percentage of Er (25%) to Fe3O4 is worth examining more closely. However, in the light of this thesis, this can be attributed to the improved magnetic susceptibility as Er is added to Fe3O4 in such a manner that when excessive amounts of Er are added, the sample tends to aggregate and this aggregation hinders the ability of the sample to absorb magnetic energy.
Chapter 6: Conclusion

In this chapter, a summary of work conducted and conclusions made from results is presented along with recommendations for future work.

6.1 Experimental Conclusions

Ten different formulations of MNPs were prepared and heated in a magnetic coil under dry and water dispersed conditions. Out of the 10 MNP types, Fe₃O₄ and Fe/Er 75-25 (75% Fe₃O₄ and 25% Erbium) generated the greatest temperature rise and were further tested. Different compositions of Fe/Er samples were prepared to examine the effect of Er % (75% Er, 50% Er, and 25% Er). The prepared Fe₃O₄ and Fe/Er samples were characterized for size using the nanosizer and SEM images, which showed a close match and confirmed accuracy of nanosizer results. XRD tests revealed the crystalline nature of Fe₃O₄ and its tendency to lose crystallinity as a greater percentage of Er% is added to the Fe₃O₄ NPs. EDS tests were used to validate the preparation of the NP samples and revealed a close match between intended chemical composition and actual composition confirming adequate sample preparation techniques. SQUID tests revealed a very strong magnetization of the Fe/Er 75-25 sample and confirmed that its blocking temperature exists above the test limit of 27°C. The coercivity of the sample was also computed to be around 68 Oe. However, due to the limited magnetic field of the test, saturation magnetization was not revealed, hence it was not possible to calculate the hysteresis power loss from the hysteresis loop.

Fe₃O₄ and Fe/Er samples were prepared then mixed in bitumen fluid to examine the effect of different parameters (NP concentration, NP size, Er %) on heating performance. Except for Fe/Er 75-25, all particles showed a negative relationship between concentration of NPs and SAR as concentration increased the SAR decreased.
This agreed with the collective behavior theory which explains that SAR-dependence on concentration depends on magnetic field geometry dependence and level of aggregation. Fe$_3$O$_4$ lay in the blocked regime (below its blocking temperature of 35°C), hence the increase in concentration caused an expected decrease in SAR. Fe/Er, samples on the other hand, lay in the unblocked regime for their Fe$_3$O$_4$; however, due to the increased level of aggregation and less presence of Fe$_3$O$_4$ content in Fe/Er 50-50 and Fe/Er 25-75 samples, the SAR decreased with concentration. For Fe/Er 75-25, its higher Curie temperature, greater abundance of Fe$_3$O$_4$, and low level of aggregation, allowed it to have an increase in SAR as concentration of NPs increased. For NP size, the results followed theory in the sense that all samples exceeded the exchange length of 27nm and thus SAR increased as size of NP decreased. As for chemical composition, EDS revealed that the optimal percentage of Er added to Fe$_3$O$_4$ to enhance its heating capability was 25% whereas any increase in Er % beyond that point caused a proportional decrease in SAR. This may be explained by the increase in aggregation level when Er % is increased.

### 6.2 Future Work

This thesis presents immense potential for continuing future work in this direction. The biggest key point to be studied more closely is understanding the mechanisms by which addition of Er to pure Fe$_3$O$_4$ enhances electromagnetic heating. Comprehensive SQUID analysis needs to be conducted on a wider range of Er % compositions and hysteresis losses need to be computed in order to compare the theoretical losses to the actual SAR values obtained. Moreover, characterization of pure Er needs to be conducted in order to understand its magnetic properties and the reasons behind its improvement of Fe$_3$O$_4$ heating performance.
In addition, other parameters that were not studied in this thesis can be tested. For instance, factors such as the combined effect of varying the applied magnetic frequency and particle size on SAR can be studied in order to optimize heating performance by these parameters. Additionally, the anisotropy of the samples may be measured in order to understand the effect of varying anisotropy on heating efficiency for different types and sizes of MNPs.

Moreover, this study faced difficulties in sustaining strong controls between tests in terms of maintaining particle size and preventing aggregation/agglomeration due to limited resources. Future work can involve better practices to do so in order to generate more accurate and reliable results.

Tackling these extra parameters and improving experimental controls can allow formulating a reservoir model that can project the increases in heavy oil recovery as a result of using magnetic nanoparticles for enhancing electromagnetic heating. Different variables (coil size, field frequency, NP types, NP sizes, type of medium, NP concentration) can be optimized in the model and field scale tests may be implemented to validate the model. If a strong model such as the one described is achieved, this can represent a major opportunity for developing electromagnetic heating enhanced by magnetic nanoparticles as an economically viable alternative to the expensive and environmentally hazardous SAGD process used for most heavy oil recovery operations today.
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