MANUFACTURE OF FERROFLUID: BASIC ASPECTS AND THE INFLUENCE OF KEY PARAMETERS ON THE PROCESS

by

Laura Lisa Vatta

A dissertation submitted in partial fulfillment of the requirements for the degree of

Master of Engineering (Chemical)

in the Faculty of Engineering, Built Environment and Information Technology
University of Pretoria
Pretoria

October 2002

Supervisor:
Prof. P. de Vaal

ABSTRACT

Title: Manufacture of ferrofluid: Basic aspects and the influence of key parameters on the process

Author: Laura Lisa Vatta

Supervisor: Prof. P. de Vaal

Department: Faculty of Engineering, Built Environment and Information Technology

Degree: Master of Engineering (Chemical)

Keywords: ferrofluid, ferromagnetic fluid, precipitation, saponification, peptization, magnetite, sedimentation funnels, wet high intensity magnetic separator, surfactant stabilisation, mathematical optimisation

A ferromagnetic liquid or ferrofluid refers to a stable colloidal dispersion or suspension of single domain magnetic particles coated by a surfactant and suspended in a carrier liquid. The ferrofluid as referred to in this dissertation is produced in three main stages: oxide precipitation and magnetite formation, saponification of the surfactant and peptization of the coated particles. Magnetite (Fe_3O_4), a ferrimagnetic material, is produced in a precipitation reaction from ammonium hydroxide and iron salt solutions. The magnetite is coated with oleic acid as the surfactant and is suspended in kerosene as the carrier liquid.

From this brief description, it appears that the process for the synthesis of ferrofluids is quite simple. However, some of the basic aspects and key manufacturing parameters are not understood fully. In this dissertation an attempt is made to explain and offer a more detailed understanding of some of the steps in the manufacture of ferrofluid.

Magnetite formation is vital for the production of ferrofluids. The formation and transformation pathways of iron oxides required to form magnetite are, however, more complex. There are many pathways that could lead to the formation of incorrect species. Possible mechanisms for the formation of magnetite are discussed. Parameters that could affect the production of magnetite are discussed and an investigation conducted to confirm what the preferred conditions are for its production. The investigations appear to provide evidence that magnetite is produced through the formation of green rust complexes. The green rust complexes are produced from ferrihydrites and iron (II) ions. Magnetite is then produced by the dehydroxylation of the green rusts. The following parameters favour the formation of magnetite: high pH, rapid addition of ammonium hydroxide solution, a rapid stirrer speed and sufficient ammonium hydroxide to ensure that the pH is in the correct range for the dehydroxylation of green rusts and for the prevention of formation of non-magnetic oxides.

After precipitation, the aqueous solution in which the precipitate is suspended contains dissolved salts. Often, in the production of ferrofluids in the laboratory, a third phase has been produced. It is suspected that organic-inorganic phase interactions that may cause this third phase are promoted in some cases by the salts in the mixture containing the precipitate. This may hinder the final organic/aqueous phase separation. In addition, the salts in solution may increase the viscosity of the product. It would therefore be beneficial to wash the precipitate to remove these salts. For water-based ferrofluid production (where the carrier liquid is water), concentration of the magnetite suspension is essential for the production of a fluid of suitable magnetic properties. Washing is also important to ensure stability of the water-based fluids.

Two methods for the washing of the precipitate were suggested. The first makes use of what have been termed sedimentation funnels. Precipitate is fed to four cone-shaped vessels in series. The funnels are plastic containers around which copper coils are wound. A direct current is passed through the coils thus generating a magnetic field in the interior of the funnel. When placed in the funnel and exposed to the magnetic field, the magnetite is attracted towards the region of greatest magnetic field and becomes concentrated at the base of the funnel. Wastewater leaves the funnels via an overflow. Computational fluid dynamics (CFD) was used to investigate the suitability of the funnel design and to determine whether the funnel configuration would ensure that the salts would be washed from the precipitate and that the magnetite would be retained in the funnels. From preliminary results obtained from the CFD model, it appears that the inflowing liquid churns up material that may have settled at the base of the funnel. It was initially recommended that the funnel geometry be modified such that the flow into the funnel does not disturb the particles at the base of the funnel. The second concept that was investigated, namely, the wet high intensity magnetic separator (WHIMS) was found to function more effectively and efforts were focused on this new concept instead.

The procedure used for the WHIMS is analogous to that of deep bed filtration with the magnetic force assisting in particle capture. The WHIMS consists of a funnel shaped vessel containing a magnetisable matrix or mesh and surrounded by a magnet e.g. solenoid electromagnet. Magnetic particles (such as the magnetite) fed to the WHIMS are captured in the matrix when the current to the coils is switched on. The liquid in which the magnetite is contained passes through the vessel. Water can be added to the vessel to wash the magnetite. An investigation was conducted on a WHIMS prototype that was built to determine whether or not it would be suitable for the purposes of washing and concentrating the magnetite. Furthermore, a qualitative estimation of the suitability of three mesh types was performed and suggestions made as to which mesh would be most suitable for use in a process to manufacture ferrofluid on a continuous basis.

The particle size of the magnetite which is one of the most important components of the ferrofluid is critical for fluid stability. Particles must be small enough not to settle or agglomerate as a result of gravitational and magnetic interaction forces. In addition to ensuring that the particle size is correct, the coating of the particles is an important factor for maintaining stability. The coating of particles prevents agglomeration that could occur as a result of Van der Waals interaction forces. An investigation into the optimum quantity of surfactant required for steric stabilisation showed that as the percentage oleic acid increases, the volume of magnetite remaining suspended above the ferrofluid appears to decrease. This was accompanied by an increase in the saturation magnetisation of the fluids.

In order to achieve a more rapid phase transfer in the peptization stage of the fluid production, heat is required to be input into the system. To obtain the maximum heat transfer at the maximum allowable temperature, the surface area in the column should be at a maximum. Mathematical optimisation using the dynamic trajectory method was applied to the formulation of this problem to determine the optimum dimensions of such a column (diameter, height and glass bead diameter) that would result in maximum heat transfer. Various scenarios were investigated. It was found that in the simple case where a recommended residence time for the mixture and a geometric diameter to height constraint are ignored, the solution converges where the height and diameter of the column are a maximum and the bead diameter is a minimum. When including the residence time considerations and the height to diameter ratio as constraints, various valid solutions were obtained for this problem.

Various aspects and key parameters of ferrofluid manufacture were discussed and investigated in this dissertation. Information was provided regarding the preferred parameters for the formation of magnetite, precipitate washing and concentration, the volume of surfactant required for coating magnetite particles and a suggestion of the optimum method for heat transfer in the peptization reaction. This information clarifies some of the aspects in the production of this intriguing substance.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude towards

- my supervisor, Prof. de Vaal for his guidance and assistance in the completion of the dissertation,
- my colleagues for their advice on the work and assistance with the editing of the dissertation,
- and very specially to my family and friends for their constant encouragement and support throughout my studies.

Furthermore, I would like to thank DebTech, a division of De Beers Consolidated Mines for its financial support of my studies.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

CFD	Computational Fluid Dynamics
FHS	ferrohydrostatic separation
VSM	Vibrating Sample Magnetometer
WHIMS	wet high intensity magnetic separator