
## Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# Para- and Dia-Magnetic Particle Flocculation in a Magnetic Field

C. Tsouris[a]; T. C. Scott[a]; M. T. Harris[a]
[a] Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

**To cite this Article** Tsouris, C. , Scott, T. C. and Harris, M. T.(1995) 'Para- and Dia-Magnetic Particle Flocculation in a Magnetic Field', Separation Science and Technology, 30: 7, 1407 — 1419
**To link to this Article: DOI:** 10.1080/01496399508010354
**URL:** http://dx.doi.org/10.1080/01496399508010354

SEPARATION SCIENCE AND TECHNOLOGY, 30(7-9), pp. 1407-1419, 1995

# PARA- AND DIA-MAGNETIC PARTICLE FLOCCULATION IN A MAGNETIC FIELD*

C. Tsouris†, T. C. Scott, and M. T. Harris

Chemical Technology Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, Tennessee 37831-6226



## ABSTRACT

An experimental apparatus has been assembled for the study of high-gradient magnetic separations of para- and dia-magnetic particles suspended in a liquid. The components of this system include a cryogenic magnet, equipment for light-intensity measurements, and a dynamic light-scattering technique for transient particle-size measurements. The flocculation of paramagnetic hematite particles of approximately 200-nm diameter under the influence of a uniform magnetic field is experimentally investigated. The effect of solution pH on particle growth as a result of flocculation is examined with and without the presence of the magnetic field. Results show that the flocculation rate of hematite particles increases with the intensity of the magnetic field.

## INTRODUCTION

The magnetic susceptibility of elements and compounds offers an opportunity for separations of a wide range of materials. Common applications requiring only low

---

*Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

magnetic-field strength include recovery of ferrous metals. Weakly magnetic materials may also be separated in applications requiring very strong magnetic fields. The recent introduction of high-temperature superconductors makes these applications more practical and more competitive.

Materials may fall into three general classes with respect to their response in a magnetic field: ferromagnetic or strongly magnetic materials (e.g., metals or compounds of iron, cobalt, nickel, and rare earth elements); paramagnetic or weakly magnetic materials (e.g., metals and compounds of some transition elements); and diamagnetic materials, which are weakly repelled by a magnetic field (e.g., metal and compounds of the light elements; noble metals; almost all organic compounds; and almost all gases except oxygen, nitrogen dioxide, and some other gases which are paramagnetic).

The intensity of magnetization or the magnetic moment per unit volume of a substance, M, is directly proportional to the magnetic field, H: $M = xH$ where $x$ is the magnetic susceptibility (1). A dimensionless magnetic susceptibility, $\bar{x}$ is defined as the magnetic susceptibility divided by the magnetic permeability of vacuum. Paramagnetic materials have relatively small positive values of $\bar{x}$ in the order of $10^{-3}$ to $10^{-5}$. Diamagnetic materials have relatively small negative values of $x$ in the order of $10^{-5}$. Ferromagnetic materials have large positive values of $\bar{x}$.

In many processes, colloidal particles suspended in aqueous solutions have to be removed or selectively recovered. When a colloid is exposed to a magnetic field, the following interaction forces apply among the particles: (a) attractive van der Waals forces of molecular origin, (b) repulsive electrostatic forces due to surface charge, (c) hydrodynamic forces due to the fluid properties of the surrounding phase, and (d) magnetic forces between permanent or induced magnetic moments. The latter is the only nonspherically symmetric interaction between two particles and depends on the angle between the interacting magnetic dipole moments. In principle, by adjusting the strength of the magnetic field, one can achieve flocculation of particles of certain magnetic susceptibility. The clusters of particles that are produced by flocculation can be easily removed either by sedimentation or filtration, and therefore selective separation can be attained.

Flocculation of weakly magnetic minerals has been theoretically studied by Svoboda (2,3), who examined the relative effect of attractive and repulsive forces acting on colloidal particles. The same author studied the flocculation rate in terms of a stability ratio which includes all forces applied on the particles. Similar studies have been conducted by Janssen and coworkers (4,5) with the difference that these researchers treated the magnetic force as a nonspherically symmetric interaction. In their experiments, Janssen et al. (4) studied the time-dependent extinction of light that is incident along the magnetic field. From light-extinction measurements, they determined flocculation rates of single particles into doublets. Other theoretical studies on magnetic flocculation have been reported by Wilhelm (6), Parker et al. (7), and Williams and Jia (8). Williams and Jia (8) developed a Monte Carlo simulation model that overcomes the difficulties introduced by the directional property of the magnetic force.

In the present work, an experimental study of magnetic flocculation is reported. Particle flocculation is verified qualitatively by means of light-intensity measurements. The growth of the average particle size is also measured by a dynamic light-scattering technique. While forward-light-intensity data can be used for the estimation of flocculating rate (4), light-scattering data can be used to provide direct information about the state of the particles, i.e. size and number concentration. In this respect, the experimental apparatus described here is more advanced than the ones in the cited references.



## EXPERIMENTAL

### Apparatus

The experimental apparatus is shown in Figures 1 and 2. A cryogenic magnet from American Magnetics Inc. is shown in both figures. The magnet is of split-coil design with "warm-bore" optical access in the vertical direction and every 90° in the horizontal plane. The coil is made of superconducting wire (niobium/titanium) and is driven by a high amperage power supply (model IPS-100, Cryomagnetics Inc.). Under liquid helium conditions (4.2 K), it can provide a uniform magnetic field of strength as high as 6 T. During operation, the superconductor must be immersed into liquid helium, the level of which is monitored by a liquid helium level meter (model 110, American Magnetics Inc.). The liquid helium is at the boiling point (4.2 K), and the vaporization rate is minimized by maintaining a vacuum of less than

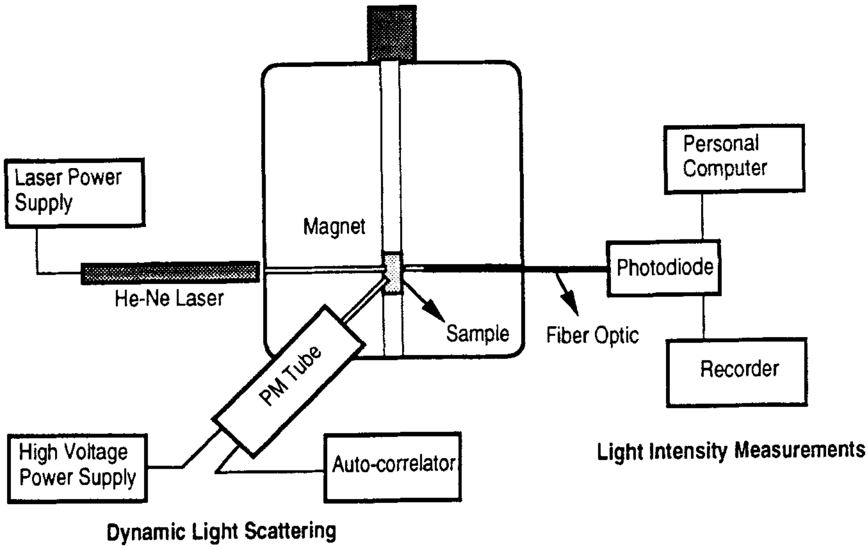


Figure 1. Experimental apparatus for magnetic flocculation.

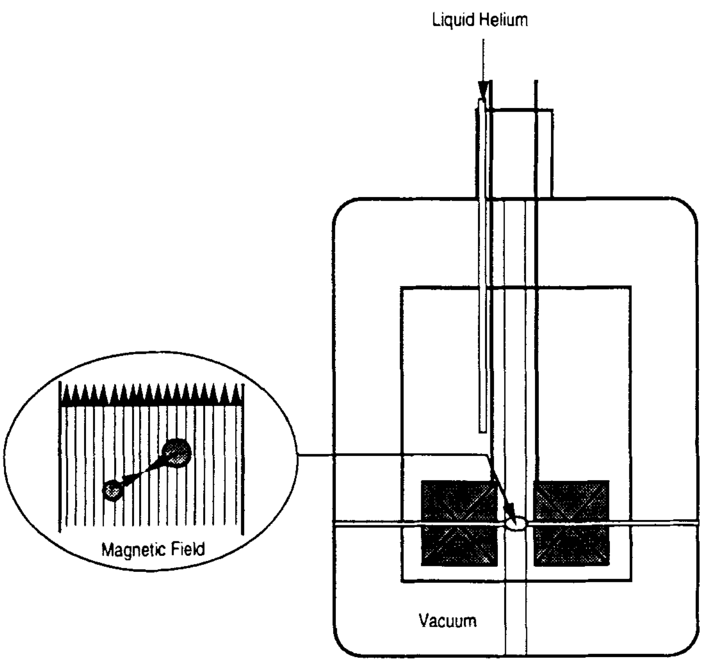


Figure 2. The cryogenic magnet.

$10^{-5}$ torr between the inside and outside walls of the magnet container (see Figure 2). Prior to the introduction of liquid helium, the superconductor is precooled by liquid nitrogen at 77 K for the reason that liquid nitrogen is cheaper and has a larger heat capacity than liquid helium.

The components of the measurement techniques are also shown in Figure 1. A 15-mW He-Ne laser is used as a light source. The dynamic light-scattering technique consists of a high-voltage power supply (model 204, Pacific Instruments), with pulse amplifier discriminator (model PAD-1, Langley-Ford Instruments), a photomultiplier tube (PMT) (model 3262RF,P, Pacific Instruments), and a correlator (model 1096, Langley-Ford Instruments). Light-intensity measurements are also obtained, at 180° with respect to the incident light, by a photodiode electronic system which translates the laser light into current and then into voltage. The signal is sent to a recorder and simultaneously sampled and stored by a personal computer. Finally, zeta-potential measurements are obtained by a Laser Zee Meter (model 501, Pen Kem Inc.).



## Procedure

Ferric oxide (hematite) powder (Baker Chemical) is used in the experiments described herein. A suspension of 1 g/L is initially made and used for the preparation of lower concentration suspensions. Suspensions of different pH and ionic strength are also prepared. The ionic strength (I) is set by adding NaCl, while the pH is adjusted by adding NaOH or HCl. Following preparation, the zeta-potential is measured by the Laser Zee Meter. For the flocculation experiments, samples of approximately 20 mL are used. These samples are first sonicated in a water bath for 10 min. The magnetic-field strength is adjusted by the IPS-100 magnet power system, and, once the field reaches steady state, the sample of the suspension is introduced from the bottom at the measuring point shown in Figures 1 and 2. The center of the magnet container along its length, including the measuring point, is thermally insulated by vacuum so that the sample temperature remains constant. As soon as the sample is placed in the magnetic field, data acquisition by a personal computer is initiated.

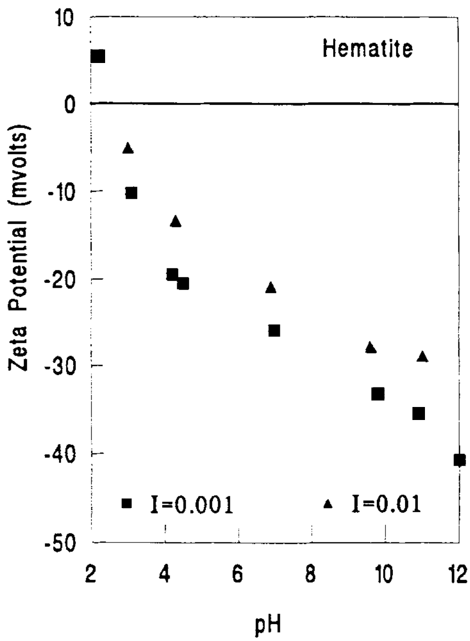


Figure 3. Zeta-potential measurements for hematite; the ionic strength, I, is adjusted by addition of NaCl; the pH is adjusted by addition of NaOH or HCl.



## RESULTS AND DISCUSSION

Zeta-potential measurements of hematite particles are shown in Figure 3 for two ionic strengths. Although a pH 8 has been reported by other investigators (9) as the point of zero charge (PZC) for hematite, a PZC of pH 3 is shown in Figure 3. This discrepancy is likely due to anions becoming attached at the surface of the particles during production.

### Flocculation in the Absence of Magnetic Field

Light-intensity measurements have been obtained at 180°, with respect to the incident light, for concentrations of particles in the range of 50-200 mg/L. These

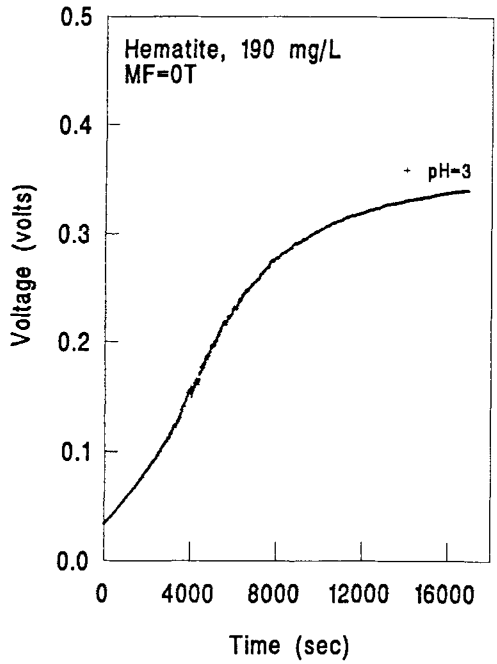


Figure 4. Light-intensity measurements during particle flocculation at the pH of zero charge with no magnetic field applied.



measurements are used to qualitatively show the effect of pH and magnetic field upon particle flocculation. The same light source is used for dynamic light-scattering measurements at 90° with respect to the incident light. The dynamic light-scattering technique provides quantitative measurements of particle size for low-concentration particles, in the range of 1-5 mg/L, at which multiple scattering is limited.

Light-intensity measurements at pH 3, at which maximum flocculation rate is expected, are shown in Figure 4. The initial part of the data shown in this figure (up to 3000 s) is due purely to particle flocculation since the particles are of nanometer size and therefore have relatively small settling velocity. The increasing voltage with time reflects the fact that higher-intensity light is passing through the sample.

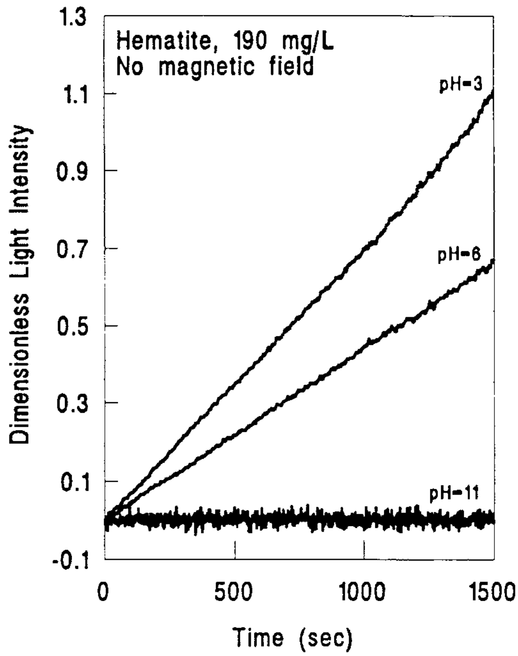


Figure 5. Effect of pH on particle flocculation with no magnetic field applied; the light intensity is normalized by the initial measurement.



Dimensionless light-intensity data, defined as of the difference of the voltage measurement at any time and the voltage at time zero divided by the voltage at time zero, are shown in Figure 5. The flocculation rate is shown to decrease with increasing pH, in agreement with the zeta-potential measurements of Figure 3. As the pH is increased, the surface charge and the electrostatic repulsive forces are increased, inhibiting flocculation. Similar results are shown in Figure 6, where the dimensionless particle diameter from the dynamic light scattering is presented at different pHs. The dimensionless particle diameter is defined as the average particle diameter at any time divided by the average particle diameter at time zero.

Flocculation in the Presence of Magnetic Field

Light-intensity measurements at pH 11 and at various values of the magnetic field, ranging from 0 to 6 T, are presented in Figure 7 with data for no magnetic field

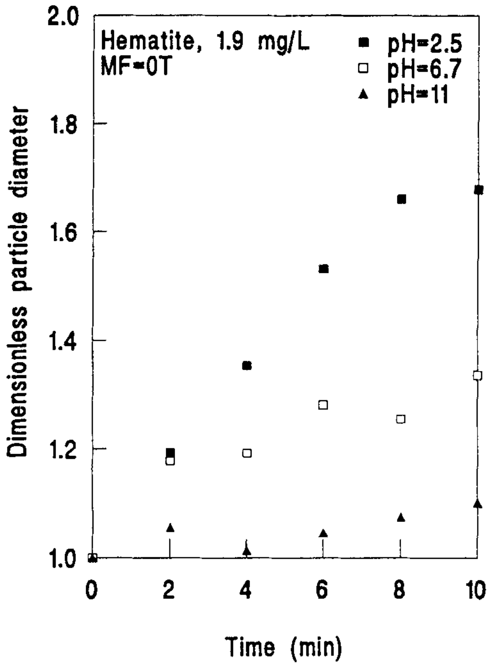


Figure 6. Effect of pH on particle growth with no magnetic field applied; the particle diameter is normalized by the initial measurement.



and zero-surface charge. From the data of Figures 7 and 5, it is clear that the stronger the magnetic field, the higher the flocculation rate. The effect of zero surface charge (pH 3) is equivalent to the effect of a magnetic field between 4.5 and 6 T. The transient dimensionless particle diameter, as defined above, is presented in Figure 8 for different intensities of the magnetic field. The average particle diameter increases rapidly at the highest intensity of the magnetic field.

## Diamagnetic Particles

Hematite is a paramagnetic material with small positive magnetic susceptibility. Diamagnetic materials, on the other hand, have small but negative magnetic susceptibility. Friedlander et al. (10) reported magnetic separation of diamagnetic

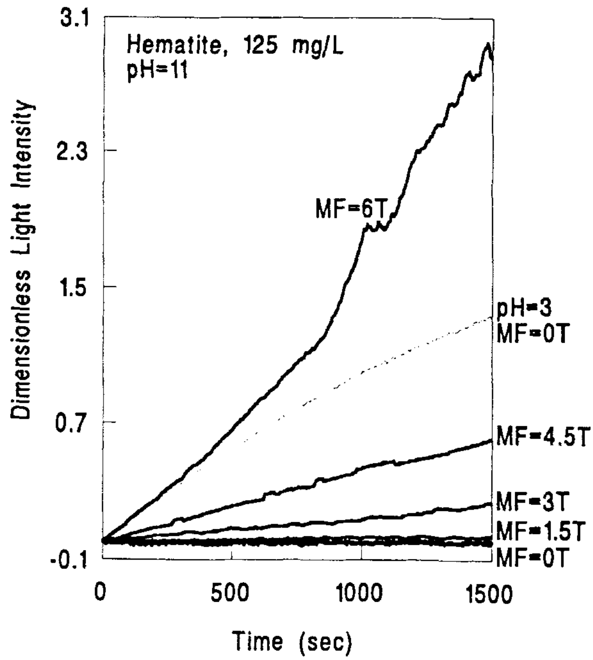


Figure 7. Effect of magnetic-field strength on particle flocculation.



particles by a ferromagnetic wire after adding a paramagnetic salt to the solution. This idea was attempted in this work; diamagnetic polystyrene particles were suspended in 15 wt % $MnCl_2$ (paramagnetic salt). The high salt concentration eliminated the repulsive electrostatic forces, therefore, addition of a surfactant was required to stabilize the suspension. Two experiments, conducted under a 6 T magnetic field, are presented in Figure 9. The addition of paramagnetic salt seems to have no effect on the stability of the colloid even at maximum strength of the magnetic field. This behavior, however, may be a result of the surfactant that has been added to the system. In future experiments, the behavior of diamagnetic particles in the presence of ferromagnetic material will be studied.

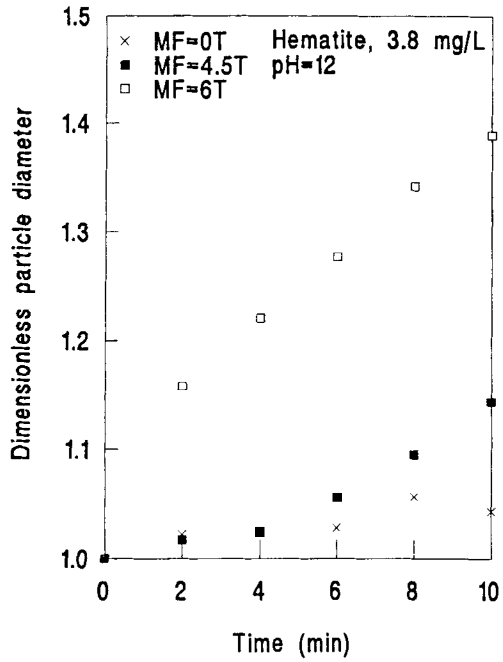


Figure 8. Effect of the magnetic-field strength on particle growth; the particle diameter is normalized by the initial measurement.



## CONCLUSIONS

The present study deals with flocculation of weakly magnetic particles in high-intensity magnetic fields. An experimental apparatus consisting of a cryogenic superconducting magnet and measurement techniques based on laser light scattering have been developed. Hematite-particle flocculation is monitored by light-intensity measurements obtained at 180 and 90° with respect to the incident light. Results show qualitatively the effects of the magnetic field and the pH on particle flocculation. The magnetic field appears to play an important role in particle flocculation, especially in the range of 4.5-6 T. A quantitative analysis on flocculation

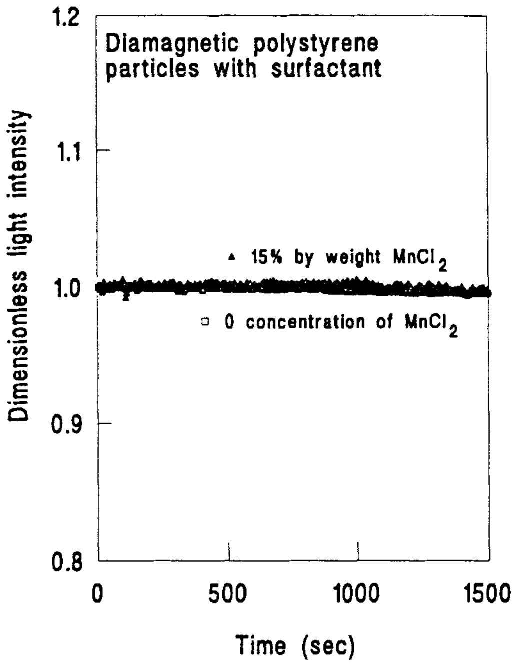


Figure 9. Flocculation measurements of diamagnetic particles; the light intensity is normalized by the initial measurement.



of paramagnetic particles, that takes into account all interparticle forces, is presented elsewhere (11).

## ACKNOWLEDGMENTS

Funding through the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., is gratefully acknowledged. This research was supported in part by an appointment to the Oak Ridge National Laboratory (ORNL) Postdoctoral Research Associate Program, administered jointly by ORNL and Oak Ridge Associated Universities. Also, the authors are thankful to Mr. W. G. Sisson for his valuable contribution during the execution of the experiments and to Ms. J. S. Taylor for her contribution in the preparation of this article to its final form.

## REFERENCES

1. S. Chikazumi, Physics of Magnetism, J. Wiley and Sons, Inc., NY (1964).

2. J. Svoboda, Int. J. Miner. Process. 8, 377 (1981).

3. J. Svoboda, IEEE Trans. Magn. Mag-18(2), 796 (1982).

4. J. J. M. Janssen, J. J. M. Baltussen, A. P. van Gelder, and J. A. A. J. Perenboom, J. Phys. D: Appl. Phys. 23, 1447 (1990).

5. J. J. M. Janssen, J. J. M. Baltussen, A. P. van Gelder, and J. A. A. J. Perenboom, J. Phys. D: Appl. Phys. 23, 1455 (1990).

6. H. E. Wilhem, Phys. Fluids 29(5), 1441 (1986).

7. M. R. Parker, R. P. A. R. van Kleef, H. W. Myron, and P. Wyder, J. Colloid Interface Sci. 101, 314 (1984).

8. R. A. Williams and X. Jia, Int. J. Miner. Process. 33, 175 (1991).

9. L. Liang, Effects of Surface Chemistry on Kinetics of Coagulation of Submicron Iron Oxide Particles ($\alpha$-$Fe_2O_3$) in Water, Ph.D. Thesis, California Institute of Technology, 1988.

10. F. J. Friedlander, M. Takayasu, and T. Nakano, IEEE Trans. Magn. Mag-15(6), 1526 (1979).

11. C. Tsouris and T. C. Scott, J. Colloid Interface Sci. (to be submitted).