

**APPLICATION OF NANO PARTICLES TO FINE COAL FLOAT
SINK TESTS**

ACARP Project C20044

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November 2013

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ABSTRACT

The elimination of organic chemicals, used in float/sink testing from laboratories is a priority for the Coal Industry. A variety of replacements are under investigation including ferrofluids, zirconium dioxide and caesium formate. This project initially investigated the application of magnetorheological (MR) fluids to float sink testing. MR fluids contain ferromagnetic particles which are too heavy for Brownian motion to keep in suspension. Modelling indicated that a ferrofluid layer of homogeneous density could be achieved by application of an alternating magnetic field at a certain frequency. The frequency will cause the magnetic domains to flip and hence hold them in a fixed position in space. This frequency is thought to be in the kilohertz region. Experiments were conducted; however, the apparatus was unable to generate the required frequency and field strength. Hence the theory could not be validated. It was also determined that to build a system to achieve the required magnetic field would be beyond the project budget.

Consequently, the project then focussed on completing the experimental work using DC magnetic fields for both MR and colloidal type ferrofluids. A colloidal type ferrofluid is a solution containing ferromagnetic nanoparticles that are suspended by Brownian motion and hence do not settle or clump at the pole face when subjected to a magnetic field. The result of the application of the magnetic field is a change in the apparent density due to a change in buoyancy. A series of experiments were performed using density tracers and ferrofluids subjected to varying magnetic field strengths. The experiments were to place density tracers in the ferrofluid and to increase the magnetic field strength acting on the ferrofluid. The results were that as the magnetic field strength was increased the tracers rose to the surface of the ferrofluid and were recovered. Figure 1 shows the density of the recovered tracers as a function of the applied magnetic field strength. The experiments confirmed that density control was possible with the float/sink status of a tracer being able to be controlled through changes in the strength or the applied magnetic field.

Future work is required to determine the practicality of using ferrofluid to separate coal samples. The key issues to evaluate are cleaning of ferrofluid from the coal particles (including ease/method of cleaning and adhesion of the ferrofluid to the coal particles), viscosity, and costs and “sharpness” of the float/sink cut point.

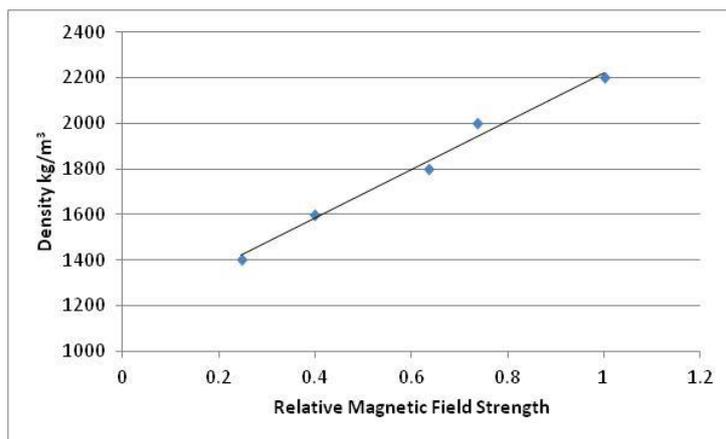


Figure 1- Recovered tracer density as a function of applied magnetic field

EXECUTIVE SUMMARY

PROJECT OBJECTIVES

The elimination of organic chemicals from laboratories is a priority for the Coal Industry. A variety of replacements are under investigation including ferrofluids, zirconium dioxide and caesium formate. This project proposed to use ferromagnetic nanoparticles in a laboratory fine coal separation.



Figure 2 Fine Coal Separation

Fine coal ($<2\text{mm}$) is currently separated in the laboratory using flasks filled with heavy liquid as shown in Figure 2. The aim of this project was to modify this procedure by the addition of a computer controlled magnet array and the replacement of the heavy liquid with ferromagnetic nanoparticles (e.g. magnetite, Permalloy, carbon coated cobalt etc) and a liquid (e.g. water, kerosene etc). The small nanoparticles could be held in suspension in a band in a controlled manner from relative densities of >1 to 2.2. Figure 3 describes that the intent was to provide a visual separation of the float and sinks.

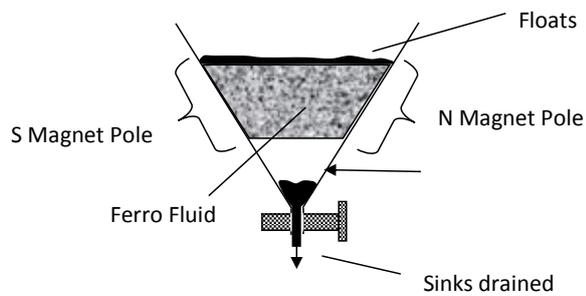


Figure 3- Original aim was to provide a visual separation

The key advantages for this method are:

- Elimination of toxic organic chemicals from the fine coal float sinking process
- Lowering of safety and environmental risk
- Ability to select any particular density by altering magnetic field.
- Small machine footprint
- Freeing of any trapped pyrite or paramagnetic particles
- Ferro-fluids complement other alternate technologies such as zirconium dioxide and caesium formate which are better suited for coarse coal.
- Ability to manipulate nanoparticles for visual separation
- Negligible machine maintenance due to absence of moving parts
- Inherent shielding and electrical magnets prevent stray magnetic fields.
- Lend itself to automatic control and subsequent lowering of operating costs

MAIN FINDINGS AND CONCLUSIONS

Modelling indicated that a stable density band could be achieved by application of an alternating magnetic field at a certain frequency to an MR fluid. The frequency will cause the magnetic domains to flip and hence hold them in a fixed position in space. This

frequency was thought to be in the kilohertz region. Experiments were conducted - however the apparatus was unable to generate the required frequency. Hence the theory could not be validated. As that late stage of the project the cost of the equipment to a system to achieve the required magnetic field was beyond the current project budget. The theory has yet to be proven.

The project team then looked at colloidal type ferrofluid and the use of buoyancy control to change the apparent density (Svoboda, 2004). Experiments were conducted and control of the density via control of the applied magnetic field was demonstrated. Literature indicated that control in the densities range of 1200 -2200 kg/m³ is difficult because of the specific requirements for the applied magnetic field. The specific requirements being the feasibility of generating an appropriate gradient field over a volume large enough to accommodate a number of coal particles.

Future work in this area will require design and construction of apparatus to test the theory of density control of MR fluids and/or to develop equipment to generate magnetic fields to provide homogeneous stable apparent density control of a colloidal ferrofluid.

INDUSTRIAL APPLICATIONS

The colloidal nature of ferrofluid enables the formulation of solutions of any density with the apparent density of the ferrofluid able to be increased to >2200 kg/m³ by the application of a magnetic field. These properties enable the industrial application of ferrofluid to float/sink testing. This would be achieved by using the ferrofluid solutions as a direct replacement for heavy liquids. The procedure would:

- a. place the coal particles in the lowest density ferrofluid solution
- b. recover the floats, rinse and dry
- c. apply a magnetic field to the ferrofluid so that the sinks float
- d. recover the floats, rinse and place in the next higher density ferrofluid
- e. repeat from step b. above

The evaluation of this technique requires further study including an experimental program to be undertaken at a coal laboratory in a comparative study with conventional heavy liquid separation.

RECOMMENDATIONS

Future work in this area will require design and construction of apparatus to test the theory of density control of MR fluids and/or to develop equipment to generate magnetic fields to provide homogeneous stable apparent density control of a colloidal ferrofluid.

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Colloidal type ferrofluid with densities equivalent to heavy liquids currently used in float sink testing should be acquired. A rare earth magnet should also be acquired. Some of the key issues to evaluate would be cleaning of ferrofluid from the coal particles (including ease/method of cleaning and adhesion of the ferrofluid to the coal particles), viscosity, costs and “sharpness” of the float/sink cut point. A comparison of the performance of the ferrofluid and the organic heavy liquids should also be made.

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The sinks in the ferrofluid will be recovered by placing the ferrofluid containing the coal onto the rare earth magnet. This will increase the apparent density sufficient enough to cause the sinks to float and allow recovery.

If it is demonstrated that the characteristics of ferrofluid are suitable for float sink testing then automatic control of the full range of required densities using magnetic fields and a single container of ferrofluid could be implemented.

REPORT

The elimination of organic chemicals from laboratories is a priority for the Coal Industry. A variety of replacements are under investigation including ferrofluid, zirconium dioxide and caesium formate. This project proposes to use ferromagnetic nanoparticles in a laboratory fine coal separation. The project outcome will be an evaluation of a prototype float sink separation procedure/device.

Fine coal (<2mm) is currently separated in the laboratory using flasks filled with heavy organic liquid. This method will be modified by the addition of a computer controlled magnet array and the replacement of the heavy liquid with Ferro-magnetic nanoparticles (e.g. magnetite, Permalloy, carbon coated cobalt etc) and a liquid (e.g. water). The small size of the nanoparticles allows the formation of a ferrofluid layer of relative densities from >1 to 2.2.

The key advantages for this method are:

- Elimination of toxic organic chemicals from the fine coal float sinking process
- Low safety and environmental risk
- Any particular density can be selected by altering magnetic current.
- Small machine footprint
- Ability to vary density and manipulate the nanoparticles allows freeing of any trapped pyrite or paramagnetic particles
- Ferrofluids should compliment other alternate technologies such as zirconium dioxide and caesium formate which are better suited for coarse coal.
- Ability to manipulate nanoparticles provides visual separation
- Negligible machine maintenance due to no moving parts
- Inherent shielding and electrical magnets prevent stray magnetic fields.

CURRENT METHOD OF FINE COAL SEPARATION

Figure 2 shows the current method of fine coal separation using heavy liquids. The flask is filled with the solution density required, the sample is then added, agitated and allowed to separate. The stop-cock is turned so that the sink material is carefully drained from the bottom of the flask. This is then filtered and added to the next required density. The float material is also removed from the bottom of the flask, filtered and dried.

FERROFLUIDS

The aim of this project was to develop a method of float/sink separation utilising ferrofluid. Ferrofluid are fluids containing magnetic particles. When the particles are of a size where they are not held in suspension by Brownian motion the ferrofluid is classified as a magnetorheological (MR) fluids. The particles in a MR ferrofluid can be pulled out of solution

and collected at the poles of a magnet placed in proximity to the solution. In colloidal type ferrofluids the particles are kept in suspension by Brownian motion and are not able to be concentrated by exposure to the poles of a magnet. Svoboda (2004) established that mass yield for various density fractions are similar for ferrofluid separation and heavy liquid separation. DeBeers have developed a Ferro Hydrostatic Separator (FHS), based on the work of Svoboda that is not commercially available. No literature has been cited specifically on ferrofluid separation of coals of sub 3mm size and ferrofluid separation of Australian Coal types. The ferrofluid medium will utilize ferromagnetic nanoparticles. The advantages with using nanoparticles are:

- The very high magnetic susceptibility allows precise control using magnetic fields.
- Fine particle size allows low density homogeneous solutions.
- Nanoparticles do not oxidise which allows long term use in water solutions.

MR FERROFLUIDS

The initial aim of the project was to use MR ferrofluid and control the density of the ferrofluid through the application of a moving magnetic field. The reason for the use of MR ferrofluid being that the ability to concentrate the particles would facilitate a visual float/sink separation and would enable recovery/separation of the particles from the fluid medium. Modelling was performed to prove the concept and determine a suitable magnet configuration. Figure 4 and Figure 5 show the magnetic field model for the 4 pole configuration and Figure 6 the conceptual design.

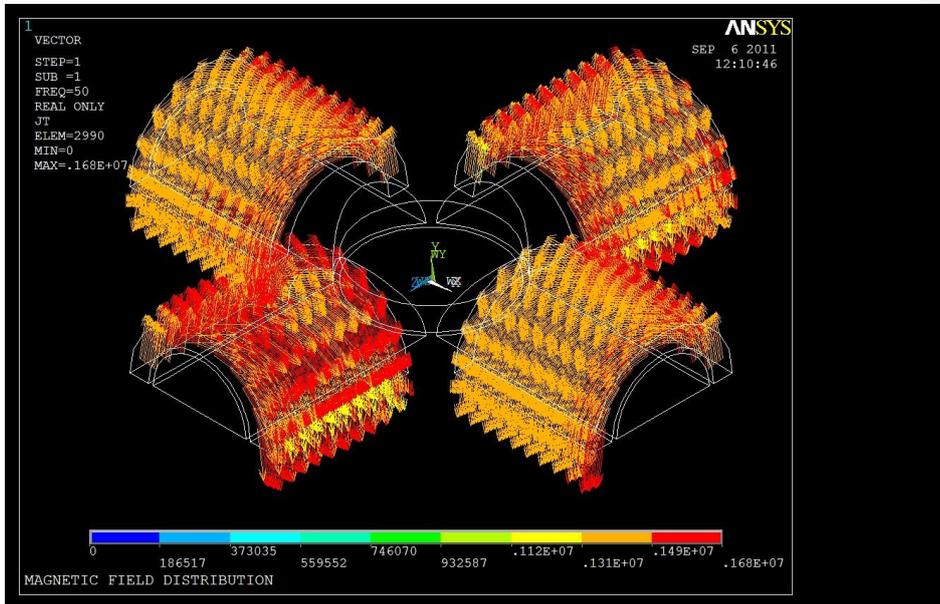


Figure 4 Simulation of 4 coil excitation

The theory demonstrated by these simulations being that the ferromagnetic particles could be held in a fixed position by the continually flipping of the magnet moments in the kilohertz range alternating field.

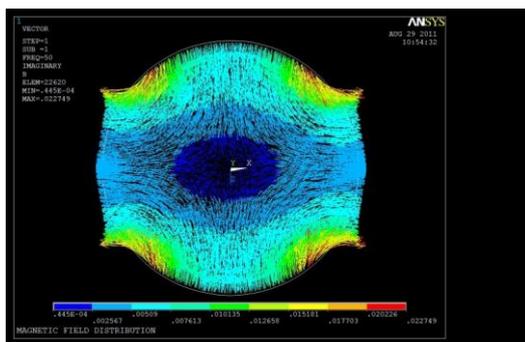


Figure 5 Simulation of 4 coil excitation

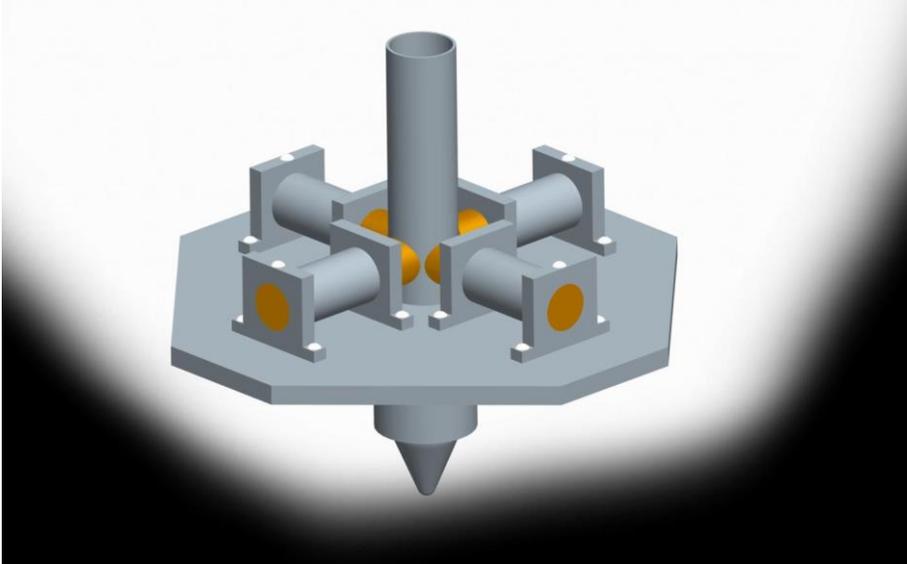


Figure 6 Conceptual design of hardware

Note the simulation shown in Figure 5 shows the central region to have a magnetic field strength many orders of magnitude less than the surrounding homogeneous field. It was anticipated the final design would require a vessel with a central void to exclude particles from this region.

The hardware was constructed (refer to Figure 7) and a power supply purchased to supply the current required to produce the alternating field. The 4 pole magnet cores were constructed of Permalloy to provide amplification of the magnetic field strength through the very high magnetic susceptibility of this material.



Figure 7 Fabricated hardware

Experiments were attempted with the hardware but unfortunately it was not possible to develop sufficient field strength and frequency to control the particles in the MR ferrofluid. Figure 8 to Figure 10 show the concentration of particles decreases as the frequency increases. It was also noted the particles rotated with the field causing turbulence. Density separation of fine particles will not be achievable in this turbulent environment. The reason for the field decreasing with frequency being the magnetic hysteresis of the Permalloy retarding the alternating field and eddy currents attenuating the field. The power supply was only able to provide a maximum frequency of 500Hz and it is apparent the particles are not held in a fixed position at and below this frequency. The cost of a power supply to develop sufficient field in the kilohertz range was beyond the remaining project budget. It was concluded that an air core DC solenoid arrangement would not be subjected to hysteresis and eddy currents and hence would be used for the next stage of the experimental work.

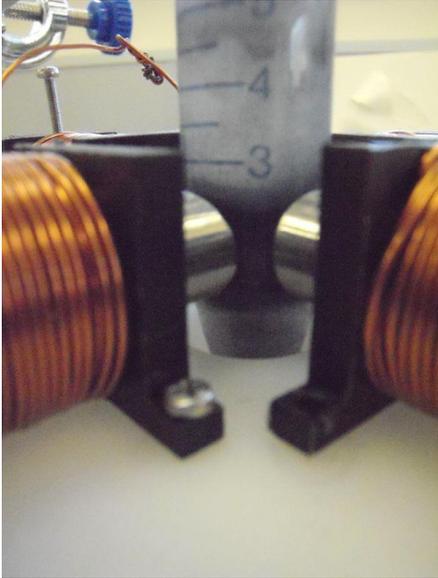


Figure 8 20Hz Applied Field

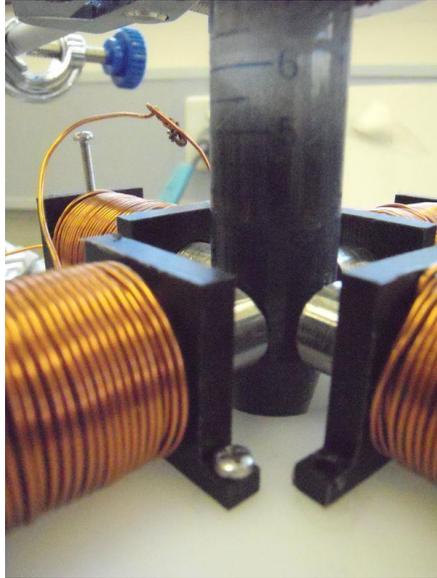


Figure 9 50Hz Applied Field

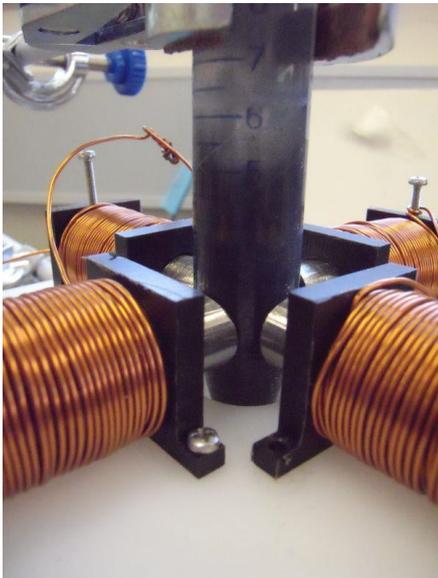


Figure 10 200Hz Applied Field

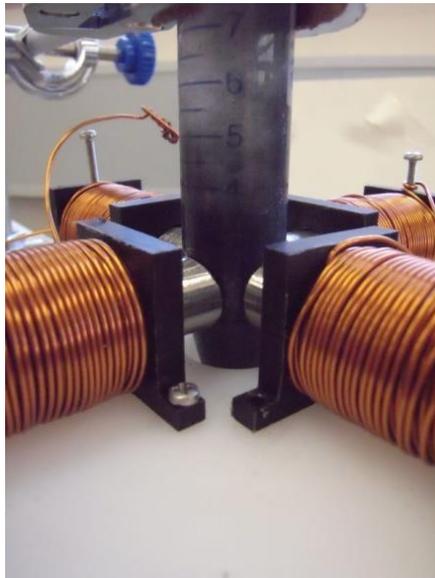


Figure 11 500Hz Applied Field

The force on a particle in a magnetic field is:

$$F = -\nabla(m \cdot B) = \frac{1}{2} \mu_0 X V \nabla(H^2)$$

where, H is the magnetic field strength (A/m)

X is the magnetic susceptibility

μ_0 is the permeability of free space ($4\pi \cdot 10^{-7}$ N/A²)

V is the volume of the particle (m³)

Thus in a uniform magnetic field ($\nabla(H^2) = 0$) there is no force on a ferromagnetic particle

In a non-uniform magnetic field the force is proportional to

$$(\nabla(H^2)) = 2H\nabla H = 2(H_x \cdot \frac{\partial H_x}{\partial x} \mathbf{i} + H_y \cdot \frac{\partial H_y}{\partial y} \mathbf{j} + H_z \cdot \frac{\partial H_z}{\partial z} \mathbf{k})$$

In other words the force is proportional to the gradient of the field multiplied by its strength.

In our design application the intention is to create a magnetic field which has $F_x = F_y = 0$ and F_z drawing the ferromagnetic particles into a band of controlled width.

Figure 12 shows the set up for the air cored solenoid experiments. Silica coated Turbo Beads were used as the magnetic particles. Note in Figure 15 Solenoid de-energised, the beads settle out of solution and are collected at the end of the funnel. The fan is to cool the solenoid as the high currents generate heat in the windings.



Figure 12 Air cored solenoid energised

Figure 12 shows that when the solenoid is energised the nanoparticles were initially uniformly distributed throughout the fluid. They are shown forming a layer within the solenoid.

Investigation revealed that this layer was not uniform across the cross-section of the tube but was rather a layer of nanoparticles on the wall.

Modelling of a finite DC solenoid show significantly reduced axial magnetic field strength and a significant non-zero tangential component of the magnetic field. This tangential magnetic field gradient component creates a force on the Nanoparticles that moves them towards the current source (solenoid windings). Figure 13 shows the nanoparticles have agglomerated and are easily seen as clumps rather than as a fine cloud. This is a characteristic of magnetorheological (MR) fluids. When MR fluids are in a magnetic field the microscopic particles align themselves along the field lines of the magnetic flux. In Figure 14 the solenoid is moved up. The nanoparticles layer does not shift with the solenoid. The vast majority of particles are not drawn back into the solenoid some time after relocation.

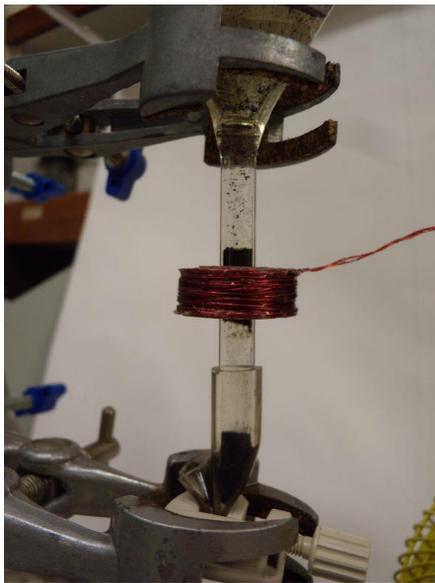


Figure 13 Solenoid energises

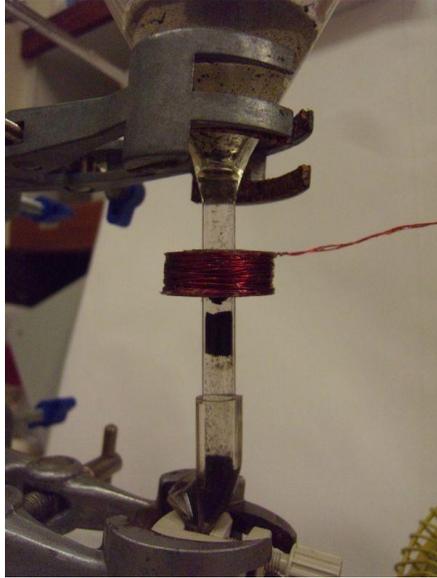


Figure 14 Solenoid moved up

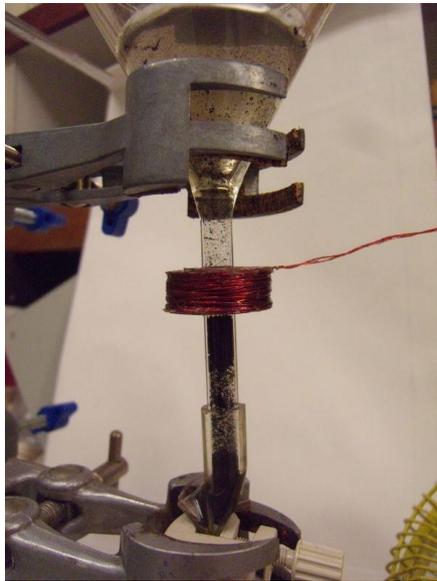


Figure 15 Solenoid de-energised

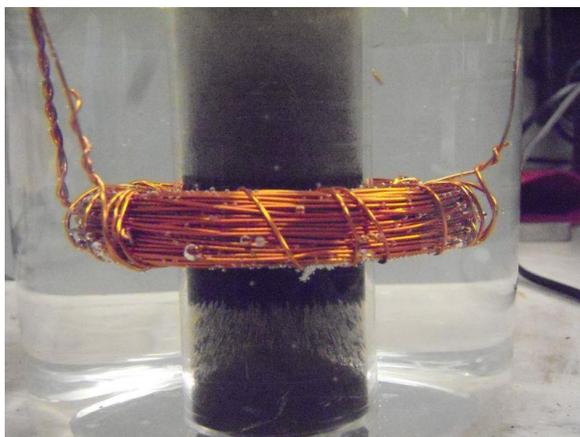
Figure 15 shows layer after the solenoid is switched OFF. Turbulence generated by the collapsing layer causes some particles to be driven upwards. Notice that the particles are still clumped – they have not dispersed with the removal of the magnetic field.

Experiments were then conducted to determine if the significance of the tangential force acting on magnetic particles can be reduced by having the solenoid diameter significantly larger than the diameter of the container (i.e. >15mm minimum distance between the particles and the coil windings) .

The large diameter solenoid set up is shown in Figure 16. The nanoparticles were initially uniformly distributed throughout the fluid until the coil was energised and then the nanoparticles formed a layer within the solenoid.

A water bath is used to reduce the rate of temperature increase of the high power density solenoid coil. (Note the bubbles forming)

Figure 16 Large diameter solenoid



After a time a stable layer is formed. Note the clumping/‘strings’ visible on the underside of the layer (refer to Figure 17).

Figure 17 Large diameter solenoid



The introduction of a density tracer of density 1.1 into the centre of the stable layer demonstrated that there was no positive buoyancy resulting from the layer.

The Nanoparticles are not uniformly distributed across the horizontal cross section of the fluid. Instead they have coalesced on the container wall (attracted to the coil windings) (see surface in Figure 18).

A large diameter solenoid (refer to Figure 19) was also tested with the same result.



Figure 18 Top view large diameter solenoid



Figure 19 Top view of a larger diameter solenoid

CONCLUSIONS OF DC SOLENOID INVESTIGATIONS

The conclusions for the solenoid experiments using MR ferrofluids are:

- MH fluids settle. Brownian motion does not keep the particles suspended.
- DC solenoids (or other static temporal field magnetic configuration) can't be used to confine the ferritic nanoparticles into a homogeneous layer because any finite (non ideal) magnetic field source will generate a force on the nanoparticles that is non vertical (in addition to the desired vertical force component). Because the ferretic nanoparticles behave like it is strongly paramagnetic it will always be attracted in the direction of maximum magnetic field gradient (field source/maximum current density/coil windings). The nanoparticles can't be magnetised so they can't be repelled by a magnetic field.
- Non-colloidal ferrofluids agglomerate in a static magnetic field, complicating attempts to produce static homogeneous density layers.
- Turbulence of the nanoparticles can easily dominate gravity/buoyancy settling. Settling only occurs in situations of minimal turbulence or bulk fluid motion.
- Ferrofluids by definition do not change density in a magnetic field. Rather density separation of non-magnetic particles is achieved by altering the buoyancy of the ferritic nanoparticles by adding a magnetic force to the gravitational force acting on these particles. In this way the density apparently changes. This concept has been successfully used for the densimetric separation of coal using magnetic fluids (J.Svoboda, 2004).

COLOIDAL FERROFLUIDS

When a colloidal ferro-nano fluid is subjected to a magnetic field the particles do not clump on the magnet pole face, as would be expected. The result of the application of the magnetic field is a change in the relative density due to a change in buoyancy. Experiments were conducted on colloidal ferro-nano fluids to ascertain whether it is feasible to use the change in apparent density in float/sink testing. Refer to Appendix 1 for ferrofluid specifications.

Figure 20 shows the apparatus used for the experiment. A container of ferrofluid is held above a rare earth magnet. The applied magnetic field is varied by adjusting the distance between the rare earth magnet and the ferrofluid. The experimental procedure was to sink a range of density tracers in the ferrofluid (i.e tracer density > ferrofluid density). The distance between the rare earth magnet and the ferrofluid was reduced resulting in tracers floating to the surface of the ferrofluid (i.e tracer density < ferrofluid density). The tracers floated to the surface in order of their density with results presented in Table 1. Figure 21 is a plot of the tracer density which floated to the surface of the ferrofluid as a function of the applied magnetic field.



Figure 20 Set up for varying magnetic field to control density

Table 1 Results for ferrofluid/tracer experiment

FerroFluid	Density at zero applied field kg/m³	Tracer Density kg/m³	Relative applied Magnetic Field
EFH1	1210	1400	0.25
		1600	0.40
		1800	0.64
		2000	0.73
		2200	1.00
EFH3	1430	1600	0.42
		1800	0.59

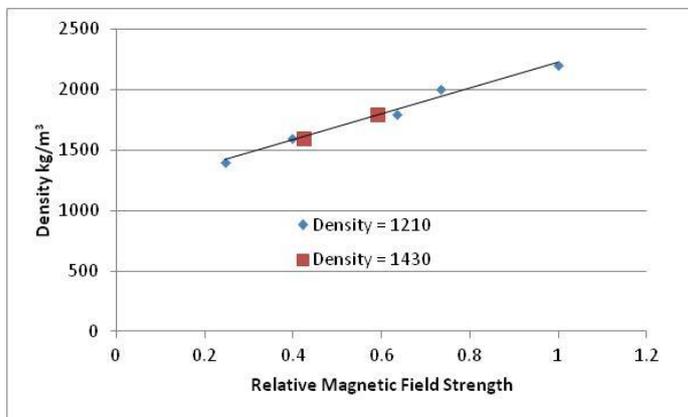


Figure 21 Float density as a function of the applied magnetic field

Industrial applications

The colloidal nature of ferrofluids enables the formulation of solutions of any density with the apparent density of the ferrofluid able to be increased to >2200 kg/m³ by the application of a magnetic field. These properties enable the industrial application of ferrofluids to float/sink testing. This would be achieved by using the ferrofluid solutions as a direct replacement for heavy liquids. The procedure would:

- a. place the coal particles in the lowest density ferrofluid solution
- b. recover the floats, rinse and dry
- c. apply a magnetic field to the ferrofluid so that the sinks float
- d. recover the floats, rinse and place in the next higher density ferrofluid
- e. repeat from step b. above

The evaluation of this technique requires an experimental program to be undertaken at a coal laboratory in a comparative study with conventional heavy liquid separation. This work will also allow the assessment of the costs of using this technique for float sink testing. The cost of the EFH1 and EFH3 used for the experimental work in this report were \$225US and \$360US per litre respectively.

RECOMMENDATIONS

Colloidal type ferrofluid with densities equivalent to heavy liquids currently used in float sink testing should be acquired. A rare earth magnet should also be acquired. A comparison of the performance of the ferrofluid and the heavy liquids should be made. The sinks in the ferrofluid will be recovered by placing the ferrofluid containing the coal onto the rare earth magnet. This will increase the apparent density to $> 2200\text{kg/m}^3$ and cause the sinks to float and allow recovery.

If it is demonstrated that the characteristics of ferrofluid are suitable for float sink testing then automatic control of the full range of required densities using magnetic fields and a single container of ferrofluid should be implemented.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the contributions to this project of the AIBN, University of Queensland and ACARP project monitors. Special thanks also to Michael Campbell of Steel River Testing for his support and advice in completing experimental work and measurements.

This project was funded by the Australian Coal Association Research Programme.

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APPENDIX 1 – FERROFLUID PROPERTIES AND MSDS