CHAPTER 5

PRECIPITATION: WASHING OF ULTRAFINE MAGNETITE PARTICLES USING A HIGH GRADIENT MAGNETIC WASHING DEVICE

1. INTRODUCTION

As mentioned in Chapter 4, ultrafine magnetite particles are produced during a precipitation reaction which forms part of the ferrofluid production process. The additional steps involved in the process which include the washing and concentration of these particles are extremely difficult. Initially the concept of four sedimentation funnels in series was investigated to perform this function and preliminary CFD modelling conducted to determine the funnels' effectiveness. The application of the concept of sedimentation funnels would require much additional work. An alternative method was investigated. This chapter documents the method selected to achieve the concentration and washing of the particles and discusses the qualitative method used to evaluate the equipment that was designed. A patent has been applied for for the concept as discussed in subsequent sections.

2. SELECTION OF A MAGNETIC SEPARATION TECHNIQUE

According to [34], magnetic separation is generally used:

- for magnetic filtration which involves the recovery of either a liquid or a solid with the magnetisable solid or liquid discarded respectively,
- for the removal of a strongly magnetisable material from a less strongly magnetisable material or
- for the concentration of a valuable strongly magnetisable material from a less strongly magnetisable material.

In the production of ferrofluids, magnetite is required to be separated from an aqueous salt solution. As mentioned in Chapter 2, magnetite adopts a ferrimagnetic ordering in a magnetic field. (In the magnetic field, the atoms magnetised in one direction have a greater effective magnetic moment than those magnetised in the opposite direction as shown in Figure 5.1.) [34]

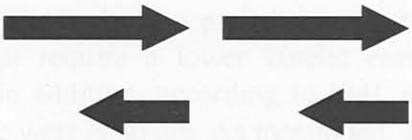

Figure 5.1 Schematic representation of spin arrangements for a ferrimagnetic ordering

There are many different types of magnetic separation technologies and the selection of the most suitable technique is not a simple task. A suggested starting point is to consider the particle size distribution. The average particle diameter of the precipitated magnetite is 10 nm. It is suggested that in the case where the magnetic particles are smaller than 75 μm, a wet separation technique is most suitable. Fine magnetic particles are usually recovered by wet intensity magnetic separators and it was therefore proposed that a wet high intensity magnetic separator (WHIMS) be used in the washing process of the nanometre-sized magnetite particles during the production of ferrofluid. [34]

3. WET HIGH INTENSITY MAGNETIC SEPARATOR DESIGN

The WHIMS is a vessel containing a magnetisable matrix which is surrounded by a magnet e.g. solenoid electromagnet. The procedure used for the WHIMS is analogous to that of deep bed filtration with the magnetic force assisting in particle capture. Sections 3.1 to 3.4 mention points that are relevant to the performance of the WHIMS. [34]

3.1 Matrix

The choice of a matrix is dependent on a number of factors: size, shape, height, loading, magnetic properties, matrix material, wear and clogging. [34]

Matrices can be characterised by their filling factor or by their porosity. A typical filling factor for expanded metal is 0.12 to 0.27 whilst that for wire mesh is in the region of 0.15 to 0.25. The matrix height should be as low as possible in order to minimise the height of the coil. The largest magnetic force should be used which implies the largest possible magnetic field. The total magnetic induction in the vicinity of the matrix element is given by the superposition of the background magnetic induction and the induction due to the matrix element. [34]

The finest possible matrix compatible with the particle size should be used to trap the maximum volume of particles. The ratio of the matrix element radius ($r_{matrix\ element}$) to the particle radius ($r_{particle}$) should preferably be between 100 and 500 but larger than 10. This is so as not to cause mechanical straining owing to particle retention which occurs when $\frac{r_{matrix\ element}}{r_{particle}} < 10$. [34]

The matrix material may be subject to abrasive, adhesive and erosive wear. Erosive wear is a function of incident conditions, characteristics of the medium passing through the matrix and the matrix material characteristics. The higher the particle size and velocity, the higher the erosive wear. Particles that are angular require a lower kinetic energy than spherical particles to penetrate the matrix material. In addition, according to [34], at 10 m/s, the threshold particle diameter so as to prevent erosive wear is 30 μm. As mentioned, the magnetite particles that are to pass through the WHIMS have an average particle diameter of approximately 10 nm and a low linear flow rate through the matrix (of the order of 1 m/s). In addition, the shape of the particles is predominantly spherical. It can therefore be expected that there should not be any problems as a result of erosive wear. An additional consideration in terms of erosive wear is the possible impact of the fluid on the matrix at the WHIMS inlet. For the application of magnetite washing, the inlet velocity at the nozzle is greater than that through the WHIMS. The liquid inlet is situated at a certain height above the mesh and the liquid does not impact directly on the mesh. The spray pattern of the nozzle is such that the liquid is distributed over the surface of the mesh. There will therefore not be any localised erosive wear on the mesh.

More serious in this application than the possibility of wear caused by the particles is the possibility of corrosion caused by the aqueous salt solution. The magnetite suspension contains chlorides which can be highly corrosive to certain metals or alloys. The WHIMS vessel should preferably be manufactured from plastic and the matrix coated to minimise the effects of corrosion whilst at the same time not affecting the magnetic properties of the matrix.

Blockage of the matrix can be minimised by:

- matching the matrix to the particle size distribution of the feed,
- by using a matrix material of low remanent polarisation (The remanent polarisation refers to a certain permanent magnetisation which remains when the magnetic field is removed. It is a function of the type of material used for the matrix – the removal of particles from the matrix will be promoted if the remanent polarization of the mesh is as low as possible.) and
- by cleaning the matrix with air or water jets. [34]

3.2 Flow velocity

The efficiency of separation is greatly affected by the flow velocity in the matrix. For successful magnetic separation, the magnetic force must be greater than the sum of all competing forces. An increase in flow velocity results in an increase in hydrodynamic drag thereby reducing separation efficiency. A compromise must therefore be reached between product recovery and throughput. The fluid shear stress on the deposited particles should be as low as possible whilst attaining a suitable throughput. [34]

3.3 Feed rate

For a continuous separation process, the higher the feed rate, the higher the throughput through the separator. This is thus an important factor in determining the cost-effectiveness of the separator. If the matrix is not flooded and the loading has not been exceeded, the interstitial velocity through the matrix is high at low or moderate feed rates. The erosion force on the deposited particles will be large. Recovery will increase with increase in flow rate because, at high feed rates, when the matrix is flooded, the interstitial velocity decreases. The grade of recovered material may, however, be lower as the content of non-magnetic material in the final product may increase. [34] For the application that was tested, the throughput was taken to be fixed. In a practical application, the WHIMS filling time, the washing cycle time and the number of washes and the flushing time would be variable.

3.4 Rinsing and flushing

For the production of ferrofluid, non-magnetic particles and salts should be rinsed from the precipitate for reasons described in Chapter 4. An increase in the volume of rinse water will usually result in a decrease in the recovery of the magnetic particles but an increase in the concentration of magnetite particles in the final product. It has been found, however, that a point is reached where increasing the volume of rinse water results in a negligible effect on the recovery of the desired material. After an initial improvement in flushing of particles from a matrix with increase in flushing velocity, a point is reached where particle removal increases only slightly with an increase in velocity. [34]

It has also been found that the removal of particles from the mesh can be dependent on the pH of the flushing water. The optimum pH is dependent on the surface properties of the captured material. Electric double-layer and London-type Van der Waals interactions probably represent the residual forces that prevent complete flushing of the matrix. [34] If the electrostatic attraction between the adsorbed particles and the matrix is neutralised, it is more likely that particles will be flushed from the matrix. Flush water of low or high pH for example will provide positive or negative charge respectively to achieve this charge neutralisation. In addition, a high pressure can be used for flushing to mechanically remove the particles from the matrix. High pressure flushing may also be required as there may be a stray magnetic field and a remanent magnetisation of the matrix. [34]

A specified volume of water is used to flush the magnetic material from the matrix. In practice, for the manufacture of ferrofluid, this volume of flush water would be recirculated through the WHIMS with the field removed so as to minimise the resultant suspension volumes. [34]

3.5 Selection of parameters for WHIMS design

3.5.1 Selection of the matrix and magnetic field strength

Optimum selection of the type of matrix and of the magnetic field strength is critical for correct and trouble-free operation of the WHIMS. Standard procedures [34] for such a selection cannot be applied to ultrafine magnetite in view of its high magnetisation and, at the same time, very small particle size.

In order to better understand the problem, a few preliminary experiments were carried out at Mintek using their laboratory WHIMS. The following combinations of the matrix type and the field strength were used:

- A mild steel woven mesh matrix of 5 mm aperture and 2 mm thick wire was placed in the residual magnetic field of the WHIMS electromagnet (170 G). Most of the magnetite was captured by the matrix but it was extremely difficult to flush the magnetite from the matrix. [35]
- An austenitic stainless steel expanded metal matrix was placed in the field of 9 kG. Not all of the magnetite was captured on the mesh. Once the field was switched off, it was easy to flush the magnetite from the matrix (at the residual field of 170 G). [35]

It thus became clear that in order to achieve capture of all the magnetite with a subsequent efficient wash from the matrix, a coarse ferromagnetic matrix with a low filling factor placed in a modest magnetic field should be used. Based on this philosophy, a solenoid magnet that could generate a magnetic field of 800 to 1000 G was designed and manufactured, based on the specifications summarised in Table 5.1. Coarse matrices shown in Figure 5.2, arranged with a low filling factor were manufactured. [35]

Table 5.1 Properties of the solenoid electromagnet

Property	Description
Inside diameter	240 mm
Outer diameter	Approximately 560 mm
Height of winding	120 mm
Number of turns	2500
Wire	Copper, diameter 2.5 mm
Length of wire	Approximately 3200 m
Resistance of winding	Approximately 10 ohm
Operating current	Maximum 10 A
Voltage	Maximum 100 V
Maximum magnetic field	800 G
Steel cladding	4 mm thick mild steel

Three types of mesh were manufactured for test work (as shown in Figure 5.2). They consist of circular sections of:

- an expanded metal sheet with 8 mm X 20 mm diamond shape openings, a gap of 2 mm between openings and a thickness of 1.2 mm (this mesh will be referred to as Mesh 1),
- a galvanised woven wire screen with a 10 mm aperture and a wire of 4 mm diameter (this mesh will be referred to as Mesh 2) and
- a high carbon woven wire screen with a 5 mm aperture and a wire of 3.15 mm diameter (this mesh will be referred to as Mesh 3).

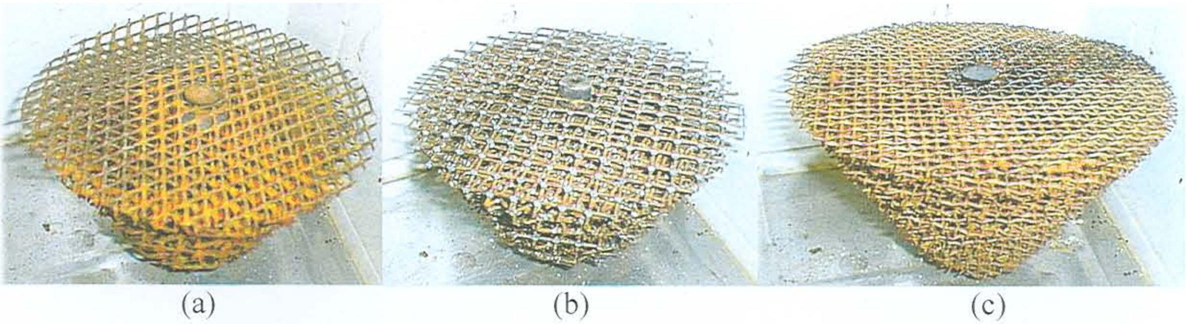
(a) (b) (c)

Figure 5.2 (a) Mesh 1, (b) Mesh 2 and (c) Mesh 3

The ratio of the matrix element and particle radii for all the mesh types is greater than the minimum recommended ratio of 10.

3.5.2 Physical arrangement of the WHIMS

The physical arrangement of the WHIMS consists of a funnel-shaped container, a section of which is surrounded by a solenoid electromagnet (see schematic cross section in Figure 5.3) and contains a magnetisable matrix. The solenoid generates a magnetic field in the funnel and the presence of the magnetisable matrix results in a high magnetic field gradient in the funnel.

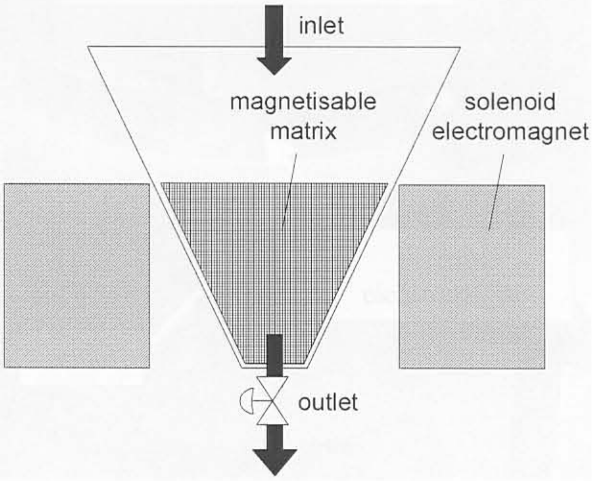

Figure 5.3 Schematic cross section of the WHIMS

A photograph of the current embodiment of the WHIMS is given in Figure 5.4 with the positioning of the matrix inside the funnel shown in Figure 5.5.

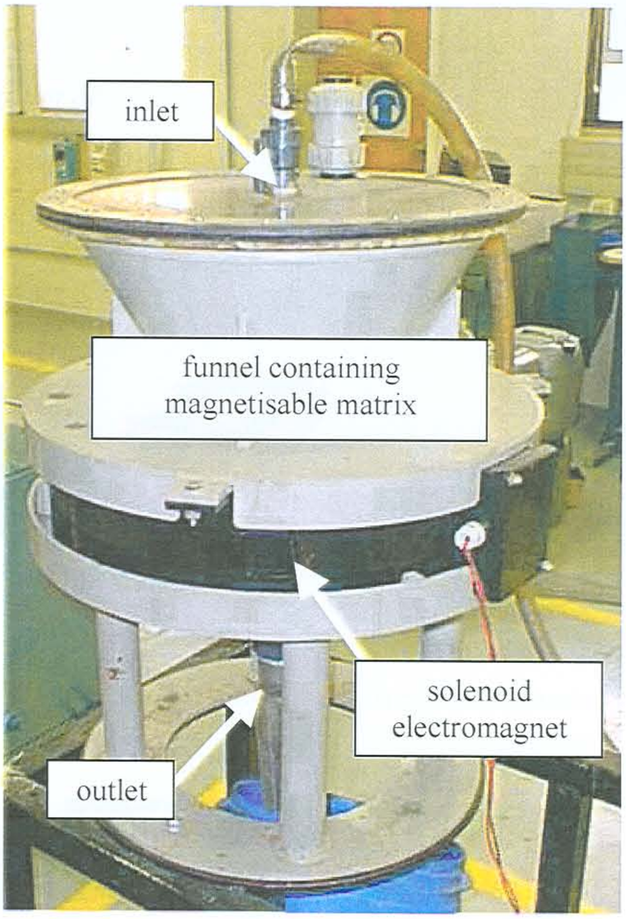

Figure 5.4 Photograph of WHIMS showing electromagnet

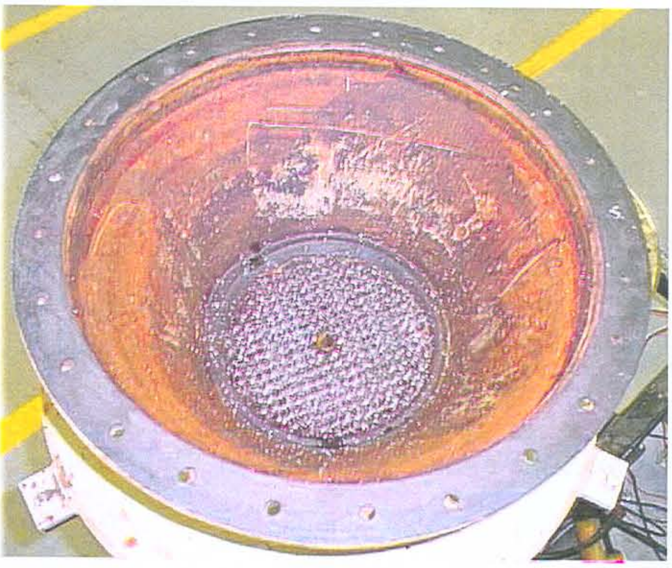

Figure 5.5 Internal view of WHIMS showing magnetisable matrix

3.5.3 Selection of spray nozzle

Two types of full cone nozzles were used for the test work. They are the FullJet and SpiralJet spray nozzle (shown in Figure 5.6) which give spray patterns as shown in Figure 5.7.


(a) (b)

Figure 5.6 (a) FullJet and (b) SpiralJet nozzles

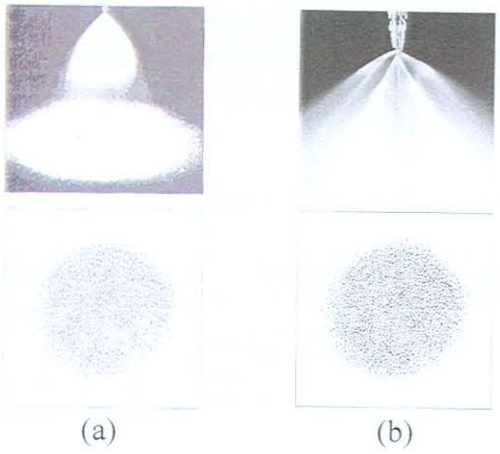
(a) (b)

Figure 5.7 Spray pattern produced by the (a) FullJet and (b) SpiralJet full cone nozzles

The SpiralJet nozzle has a larger free passage and allows for a larger capacity through the nozzle while providing complete coverage of the zone to be rinsed. It was found that the SpiralJet nozzle could flush material more efficiently from the matrix than the FullJet during preliminary test work. This nozzle was therefore used for the remainder of the testwork.

3.6 Proposed operation

A mixture of magnetite and water containing salts produced from precipitation of iron salt solution with ammonium hydroxide solution, will be passed to the WHIMS. The magnetite will be trapped on the magnetised matrix when the current to the solenoid is switched on. Water can then be passed through the matrix to wash the precipitate and remove the dissolved salts. In addition, it is likely that non-magnetic particles will be washed from the mixture. Large particles may also be washed off the matrix because of the higher force exerted on them owing to shear. Once the field has been removed, the magnetite particles can be washed off the matrix into a smaller volume of water than that in which they were originally contained and thus be concentrated.

4. EXPERIMENTAL

The WHIMS had to be tested 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 the three mesh types was to be determined. The efficiency of the particle capture of the mesh types and the particle retention on the mesh once the magnetic field had been removed had to be determined for each mesh. The results from this investigation would be used to select the most suitable mesh for operation.

A precipitate mixture was made for the test work. Table 5.2 gives the volumes that were used for the laboratory test work. A breakthrough loading was not determined as the manufacture of large volumes of precipitate in the laboratory is not practical.

Table 5.2 Volumes of reagent to be used for the test work

Reagent	Volume for test work (l/h)
$FeCl_3$ solution (43%)	0.72
$FeSO_4.7H_2O$	0.50 kg in 2 litres H_2O
NH_4OH solution (25%)	1.72

The ferrous sulphate was allowed to dissolve for 10 minutes before the ferric chloride was added. The ammonium hydroxide solution was then added rapidly to the iron solution at high stirrer speed and the resulting precipitate mixture stirred for 10 minutes.

The experimental procedure was as follows:

- Samples of 50 ml were taken from the initial precipitate mixture. These samples were labelled "a" and were used to determine the initial magnetite suspension concentration i.e. the mass of magnetite per volume of mixture as indicated by eq. (5.1). (This was performed by evaporation of the liquid and determination of the magnetite mass as explained below.)

$$Initial\ magnetite\ conc. = \frac{mass\ of\ magnetite}{volume\ of\ mixture} \tag{5.1}$$

- The initial precipitate mixture was added to the WHIMS with the current switched on.
- The mixture was allowed to drain from the WHIMS (with a certain volume of magnetite being retained on the mesh).
- The magnetite in the mixture that drains from the WHIMS while the current to the solenoid is switched on is taken to waste. This magnetite is therefore considered to be "lost". Samples of 50 ml were taken from this drained mixture. These samples, labelled "b" were used to determine the percentage magnetite that would be lost using that particular mesh as shown by eq. (5.2).

$$\%\ magnetite\ lost = \frac{conc.\ of\ magnetite\ in\ underflow\ with\ solenoid\ current\ switched\ on}{initial\ magnetite\ conc.} * 100 \tag{5.2}$$

- The current to the coils was then switched off and the mixture recirculated through the WHIMS for one minute to flush the magnetite from the matrix. The mixture that was recirculated contained the magnetite that had been "lost" in the previous step.
- After flushing, a volume of magnetite will possibly remain on the matrix as a result of the stray magnetic field, remanent polarization of the matrix and electrostatic attraction of the particles and the mesh. This magnetite may be detrimental to the process as it will result in clogging of the matrix. Samples of 50 ml of the mixture that was flushed from the matrix were taken. These samples which were labelled "c" were used to determine the percentage magnetite that was retained on the mesh after rinsing and flushing as shown by eq. (5.3).

$$\%\ magnetite\ retained = 100 - (\frac{conc.\ of\ magnetite\ in\ underflow\ with\ solenoid\ current\ switched\ off}{initial\ magnetite\ conc.} * 100) \tag{5.3}$$

- The filling of the WHIMS, the draining and the recirculating and flushing was repeated four times for each of the three mesh types (resulting in samples 1 to 4 and "a" to "c"). Between each of the repeats, the matrix was removed from the funnel and washed to ensure that the matrix was clean for the next run. The initial magnetite concentration (sample "a") for repeats 2 to 4 was taken as the concentration calculated for the percentage magnetite retained of the previous run (sample "c").
- The samples were dried in an oven and the mass of magnetite in each sample determined using a scale. The percentage magnetite lost or retained was then determined for each mesh.

The experimental setup showing the container into which the mixture was drained and the recirculation pump is shown in Figure 5.8.

Figure 5.8 Experimental setup

5. RESULTS AND CONCLUSIONS

As mentioned in Section 4, the aim of the test work was to determine whether or not the WHIMS would be suitable for the purposes of washing and concentrating the magnetite and to obtain a preliminary indication of which mesh is most suitable for the application.

The magnetite concentration in each 50 ml sample at each run is given in Table 5.3. As explained in Section 4, the percentage magnetite lost is the magnetite that is not retained by the mesh when the current to the solenoid is switched on. This percentage was determined from the sample of the underflow from the WHIMS when the current to the coil was on. The percentage magnetite retained is the magnetite that is held on the mesh when it is supposed to have been removed during the rinsing and flushing cycle. This percentage was determined from the difference between the initial magnetite concentration and the magnetite concentration of the underflow sample taken when the current had been switched off and the matrix flushed. The average percentage magnetite lost or retained for each mesh is given in the last line of Table 5.3.

Table 5.3 Magnetite losses and retention in the matrices

	Mesh 1			**Mesh 2**			**Mesh 3**		
Sample	**Fe_3O_4 conc. (g/l)**	**Fe_3O_4 lost (%)**	**Fe_3O_4 retained (%)**	**Fe_3O_4 conc. (g/l)**	**Fe_3O_4 lost (%)**	**Fe_3O_4 retained (%)**	**Fe_3O_4 conc. (g/l)**	**Fe_3O_4 lost (%)**	**Fe_3O_4 retained (%)**
1a	138.52			128.05			60.96		
1b	13.16	9.50		23.73	18.53		0.98	1.61	
1c	126.78		8.47	120.75		5.67	50.64		16.94
2a	126.78			120.75			50.64		
2b	52.46	41.31		25.40	21.03		0.49	0.97	
2c	113.94		10.14	117.62		2.60	40.19		20.64
3a	113.94			117.62			40.19		
3b	44.89	39.39		34.66	29.48		0.53	1.31	
3c	129.66		13.89	80.23		31.76	32.39		19.41
4a	129.66			80.23			32.39		
4b	41.97	32.39		16.67	20.77		0.48	1.50	
4c	108.68		16.14	60.96		24.03	22.91		29.27
Ave (%)		**30.65**	**12.16**		**22.45**	**16.01**		**1.35**	**21.56**

The initial value for Mesh 1 (run 1) for the amount of magnetite lost is significantly lower than the subsequent three values. It could be that even though the mesh was cleaned between repeats, some magnetite was still attached to portions of the mesh because of the remanent magnetisation and less surface area was therefore available for the attachment of additional magnetite. The magnetite retained also seemed to increase over time. This could also be because of the remanent magnetisation of the matrix. The magnetite retained on Mesh 2 also appeared to increase over time while the magnetite lost and retained on Mesh 3 was relatively constant.

It was found from the test work that the WHIMS will function effectively in the washing and concentration of the magnetite precipitate. As can be seen from the results, Meshes 1 and 2 behave in a similar fashion in the WHIMS while Mesh 3 loses the least amount of magnetite. Although a minimum loss of magnetite is desirable, the amount of magnetite retained on this mesh is high (approximately 22%). There is a possibility that this mesh may clog relatively easily and quickly if used in practice. Although Meshes 1 and 2 may not clog as easily as Mesh 3, they lose more than 20% of the magnetite.

6. RECOMMENDATIONS

The mass of magnetite lost is critical in producing ferrofluid of a suitable quality. The percentage magnetite retained on the three types of mesh is similar for all three cases, however, Mesh 3 exhibits the lowest loss of magnetite. It is recommended that Mesh 3 be used initially for the washing of magnetite on a larger scale. It is suspected that the outlet flow rate from the WHIMS during washing cycles could be increased with a lower loss of precipitate when using Mesh 3 as compared to the other mesh types. This implies that a greater number of washing cycles could be performed in a certain cycle time per volume if the WHIMS were used in a process that manufactures ferrofluid continuously. It is further recommended if Mesh 3 is used, that the flushing time for rinsing magnetite from the mesh be increased. If the flushing time is increased, it may be possible to wash Mesh 3 better.

If it is found that Mesh 3 clogs easily and it is not possible to remove the magnetite, Mesh 2 should be used instead. Mesh 2 loses less magnetite than Mesh 1 whilst retaining a similar percentage as Mesh 1. The flushing time when using Mesh 2 may be lower than that required to flush Mesh 3. This allows for a slower draining time or outlet velocity from the mesh which may decrease the percentage magnetite loss. The outlet velocity for the testwork was approximately 3 l/min. If this flow rate is reduced, the entrainment of magnetite out of the WHIMS may be reduced. There will be a compromise between an increase in flushing time versus a slower draining time and the number of washing cycles that can be performed. This is because the volume of the WHIMS is fixed and a washing cycle must occur within a specified period of time. Increasing both the flushing time and decreasing the outlet time may require a larger funnel.

For illustration, examples of the outlet flow rate that would be required with a specific number of washing cycles and a set flushing time are shown in Figure 5.9 (the results are represented by a curve, however, only discrete numbers of washing cycles can be performed). These scenarios are for a washing cycle with the following factors:

- an estimated total filling rate and water addition rate of 0.5 min each,
- the WHIMS has an operating volume of approximately 13 litres,
- there is a total throughput of 74 l/h in the system,
- six cycles are performed per hour (i.e. 10 minutes per cycle) and
- 12.3 litres of mixture are handled per cycle.

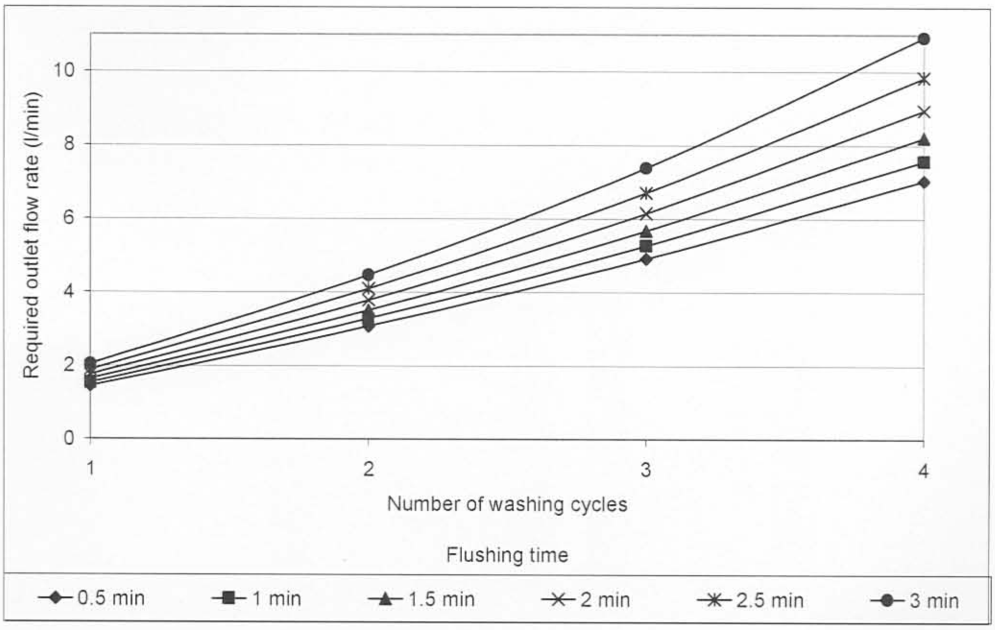

Figure 5.9 Illustration of possible scenarios for the WHIMS cycles for use in a continuous ferrofluid manufacturing process

When the actual filling rate and water addition rate have been determined, various flushing rates and numbers of washing cycles can be tested to determine the optimum manufacturing procedure.

If the current is switched on when the magnetite is added to the WHIMS, it is observed that the precipitate sometimes accumulates at the top of the WHIMS. This may be advantageous as precipitate entrained from the top of the mesh may still settle on the matrix as it travels through the matrix. It may also be disadvantageous as the surface area of the matrix will not be used to its full extent and material accumulating at the top of the matrix will not be held firmly. Furthermore, this could lead to premature blocking of the matrix. It is therefore recommended that the mixture be added to the WHIMS with the current switched off at first. Once the funnel is full, the current can be switched on. This will ensure a more even distribution of magnetite within the mesh.