

## CHAPTER 3

# THE EFFECT OF KEY PARAMETERS ON THE MECHANISM OF THE PRODUCTION OF MAGNETITE

### 1. INTRODUCTION

Magnetite formation is vital for the production of ferrofluids. A very simplified representation of the process by which magnetite is produced was given by eqs (2.11) to (2.13). The formation and transformation pathways of iron oxides are, however, more complex. There are many pathways that could lead to the formation of incorrect species. These species (with the exception of maghemite) will result in the production of a non-magnetic fluid. Although maghemite is magnetic, it may be unsuitable for other reasons. Superparamagnetic behaviour requires smaller elongated particles as compared to rounded particles. For the same particle size distribution, a fluid with rounder particles will exhibit less hysteresis than a fluid with elongated particles. When elongated particles are exposed to a magnetic field, the magnetisation vector will have a preference to lie along the elongated axis. When the field is removed, elongated particles will have to overcome an addition to the energy barrier before reversal of the vector can take place. Although maghemite is magnetic, because of shape anisotropy, its more elongated shape may result in inferior magnetic properties when used as a component of a ferrofluid. [3]

In this chapter, mechanisms for the formation of magnetite are proposed. Parameters that could affect the production of magnetite are discussed and an investigation is then conducted to confirm what the preferred conditions are for the production of magnetite and whether or not these parameters are of importance in ferrofluid production.

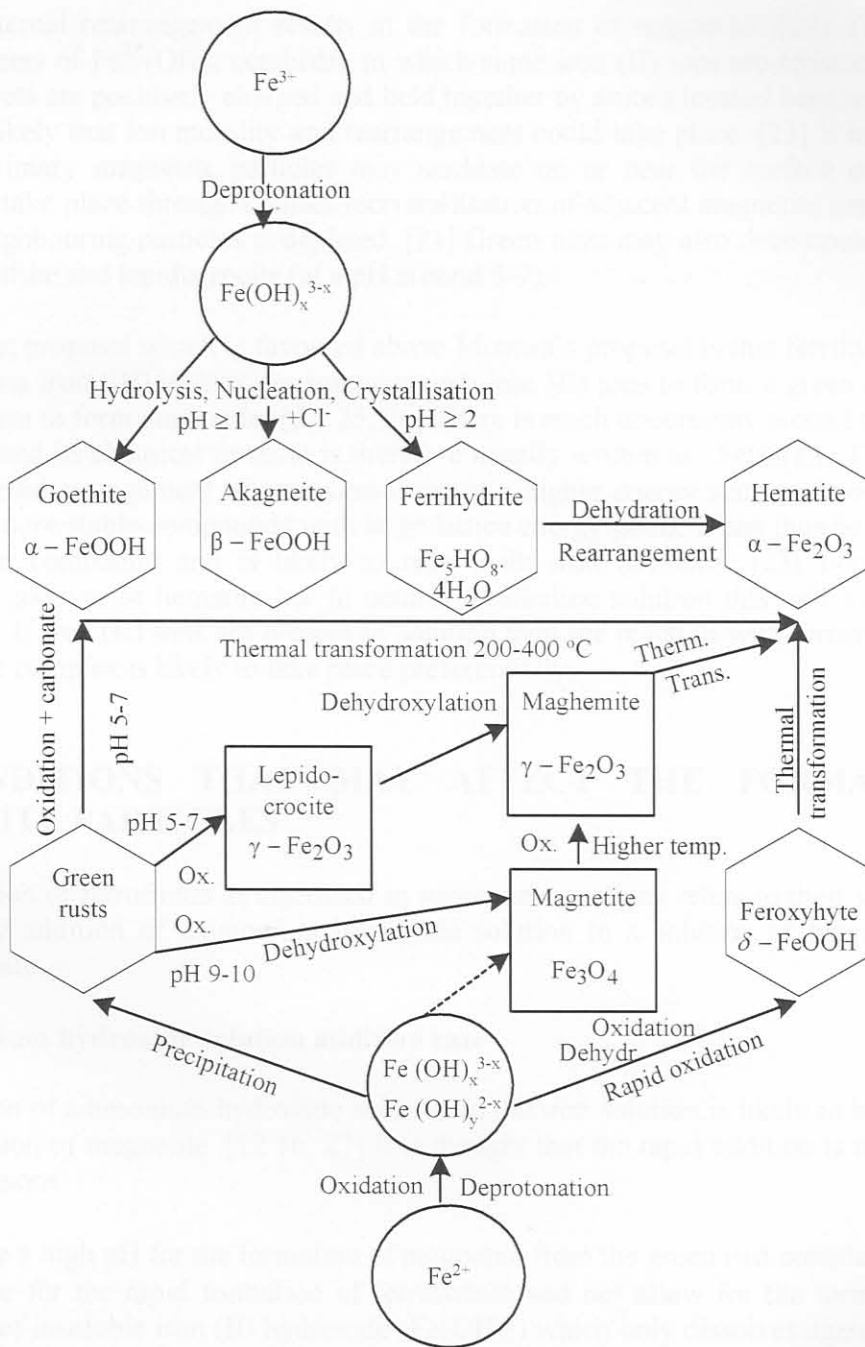
### 2. CHEMICAL PRECIPITATION OF MAGNETITE PARTICLES

Although ultrafine magnetite particles can be produced by mechanical methods such as grinding, chemical precipitation of iron oxides is the preferred method of producing magnetite as it is more rapid and offers greater control. Figure 3.1 gives a schematic representation of the possible species that can be produced from iron (III) and iron (II) ions during hydrolysis. [21]

Figure 3.1 The formation of various species from iron (II) and iron (III) ions during hydrolysis.

According to Figure 3.1, magnetite can be produced via the hydrolysis of a mixture of iron (III) and iron (II) ions.

Mitswa has proposed that when a base is added to a mixture of iron (III) and iron (II) ions, "green rust" complexes form. These green rust complexes then transform to iron (II) complexes.



**Figure 3.1** The formation of various species from iron (III) and iron (II) ions during hydrolysis

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Misawa has proposed that when a base is added to a mixture of iron (III) and iron (II) ions, “green rust” complexes form. These green rust complexes then transform to dark red complexes

before an internal rearrangement results in the formation of magnetite. [22] The green rusts consist of sheets of  $\text{Fe}^{2+}(\text{OH})_6$  octahedra in which some iron (II) ions are replaced by iron (III) ions. The sheets are positively charged and held together by anions located between the layers. It is therefore likely that ion mobility and rearrangement could take place. [23] It has been shown that small primary magnetite particles may nucleate on or near the surface of these plates. Growth may take place through contact recrystallisation of adjacent magnetite particles until the supply of neighbouring particles is depleted. [24] Green rusts may also decompose to form non-magnetic goethite and lepidocrocite (at a pH around 5-7).

A more recent proposal which is favoured above Misawa's proposal is that ferrihydrite, which is precipitated via iron (III) hydroxides interacts with iron (II) ions to form a green rust which can again transform to form magnetite. [22, 25, 26] There is much uncertainty around the structure of ferrihydrites and its chemical formula is therefore usually written as " $\text{Fe}(\text{OH})_3$ ". Ferrihydrite has a poorly ordered arrangement of atoms resulting in a higher energy state and possesses several pathways to more stable compounds with large lattice energy gains. It can thus be assumed to be a very active compound and is likely to react with iron (II) ions. [23] Ferrihydrites may transform to goethite or hematite but in neutral or alkaline solution this will most likely take place slowly. If iron (II) ions are present in solution then the reaction with ferrihydrites to form the green rust complex is likely to take place preferentially.

### 3. CONDITIONS THAT MAY AFFECT THE FORMATION OF MAGNETITE PARTICLES

The preparation of ferrofluids as discussed in subsequent sections refers to their synthesis in the laboratory by addition of ammonium hydroxide solution to a solution of ferric chloride and ferrous sulphate.

#### 3.1 Ammonium hydroxide solution addition rate

Rapid addition of ammonium hydroxide solution to the iron solution is likely to be preferred for the precipitation of magnetite. [12, 16, 27] It is thought that the rapid addition is required for the following reasons:

- to provide a high pH for the formation of magnetite from the green rust complexes,
- to provide for the rapid formation of ferrihydrite and not allow for the formation of large amounts of insoluble iron (II) hydroxide ( $\text{Fe}(\text{OH})_2$ ) which only dissolves again at high pH to form soluble  $\text{Fe}(\text{OH})_x^{2-x}$ .
- to prevent the formation of goethite and akaganeite which could result from too slow an ammonium hydroxide solution addition.

#### 3.2 Stirrer speed during precipitation

High stirrer speeds are recommended in literature for the precipitation reaction. [12] The stirrer speed is related to the pH experienced in the solution. Neutralisation of the acidic iron solution will take place more quickly if the mixture is agitated rapidly. Rapid stirring should also prevent



the formation of localised areas of high pH. In these areas, the green rust complexes will very likely form, but in other areas of low pH, non-magnetic species may be formed and non-magnetic iron oxides precipitated.

As mentioned in Section 2, small primary magnetite particles may nucleate on or near the surface of the sheets of the green rust complex and growth may take place through contact recrystallisation of adjacent magnetite particles. It is predicted that growth will cease once the supply of neighbouring particles is depleted. There may therefore be an inherent limitation to the size of magnetite crystals forming by chemical precipitation.

### **3.3 Time between precipitation and peptization reactions**

The formation of magnetite crystals from the green rust complex is governed by the kinetics of the formation of the primary particles and the contact recrystallisation. It is therefore expected that allowing some time between the precipitation and peptization reactions will maximise the formation of magnetite. As discussed in Chapter 2, the magnetite particle size is important to ensure the correct magnetic properties and to ensure stability of the fluid (by preventing settling out of particles).

### **3.4 Temperature of the iron solution before precipitation**

The precipitation of magnetite is exothermic and is accompanied by a rise in temperature in the range of 33-48 °C. If the initial iron solution temperature is high, the kinetics of the decomposition of the green rust complex may be enhanced to such an extent that smaller magnetite crystals may form.

### **3.5 Final pH as a function of the total ammonium hydroxide solution added**

According to Figure 3.1, the pH required for the conversion of green rusts to magnetite is in the range of 9-10. The amount of ammonium hydroxide solution added to the iron solution must be such that this required final pH is reached (this is on condition that the green rust complex has been produced). A volume of ammonium hydroxide solution far in excess of the final stoichiometric amount will probably be required to achieve this pH.

## **4. INVESTIGATION INTO THE PREFERRED CONDITIONS FOR MAGNETITE PRECIPITATION**

A set of investigations was designed to determine which of the parameters as discussed in Section 3 are critical for the formation of magnetite. Each of the parameters was investigated at a high and a low level. The high and low values were chosen to be at extreme conditions so that it would be more likely to observe an effect if the parameter were of importance. An attempt would be made to explain observations recorded and final results in terms of the mechanisms as discussed in Section 2.

The ammonium hydroxide solution addition rate was varied from immediate addition (in approximately one second) to addition of the solution over 20 minutes. The stirrer speed during precipitation was varied from 130 to 1300 rpm. The time between the precipitation and peptization reactions was varied from one minute to one hour. The temperature of the iron solution before precipitation was varied from room temperature (approximately 22-25°C) to 80°C. To control the final pH, the amount of ammonium hydroxide solution added to the iron solution was varied from the stoichiometric amount of ammonium hydroxide solution required for precipitation of magnetite to two times excess ammonium hydroxide solution according to eqs (2.11) to (2.13).

Whilst the parameter in consideration was varied, the other parameters were maintained constant. The constants for these parameters were chosen such that they would not adversely influence the ferrofluid production e.g. it is suspected that the ammonium hydroxide solution addition should be rapid and when the four others parameters were being investigated, the ammonium hydroxide solution addition was in one second. Five parameters were investigated at a high and low level. This would imply that ten experiments should be conducted. However, because the “constant” parameters were sometimes the same value as the high or low limit, only six investigations were necessary. This is further explained in Tables 3.1 and 3.2. In Table 3.1, the highlighted cells depict the high and low levels for the parameters.

**Table 3.1** Upper and lower limits for investigation of parameters influencing magnetite precipitation

	Ammonium hydroxide solution addition rate	Stirrer speed (rpm)	Time (min)	Temperature of iron solution	pH (final) as function of volume of ammonium hydroxide solution
1	Addition in 1 second	1300	60	Room temperature	2*excess NH <sub>4</sub> OH solution
2	Addition over 20 min	1300	60	Room temperature	2*excess NH <sub>4</sub> OH solution
3	Addition in 1 second	130	60	Room temperature	2*excess NH <sub>4</sub> OH solution
4	Addition in 1 second	1300	60	Room temperature	2*excess NH <sub>4</sub> OH solution
5	Addition in 1 second	1300	1	Room temperature	2*excess NH <sub>4</sub> OH solution
6	Addition in 1 second	1300	60	Room temperature	2*excess NH <sub>4</sub> OH solution
7	Addition in 1 second	1300	60	Room temperature	2*excess NH <sub>4</sub> OH solution
8	Addition in 1 second	1300	60	Heat iron solution to 80°C before precipitation	2*excess NH <sub>4</sub> OH solution
9	Addition in 1 second	1300	60	Room temperature	Stoichiometric amount of NH <sub>4</sub> OH solution
10	Addition in 1 second	1300	60	Room temperature	2*excess NH <sub>4</sub> OH solution

Experiments number 4, 6, 7 and 10 consist of the same conditions as number 1. These investigations were eliminated. The final investigations are depicted in Table 3.2.



**Table 3.2** Final set of investigations to determine the effect of certain parameters on the precipitation of magnetite

	Ammonium hydroxide solution addition rate	Stirrer speed (rpm)	Time (min)	Temperature of iron solution	pH (final) as function of volume of ammonium hydroxide solution
1	Addition in 1 second	1300	60	Room temperature	2*excess NH <sub>4</sub> OH solution
2	Addition over 20 min	1300	60	Room temperature	2*excess NH <sub>4</sub> OH solution
3	Addition in 1 second	130	60	Room temperature	2*excess NH <sub>4</sub> OH solution
5	Addition in 1 second	1300	1	Room temperature	2*excess NH <sub>4</sub> OH solution
8	Addition in 1 second	1300	60	Heat iron solution to 80°C before precipitation	2*excess NH <sub>4</sub> OH solution
9	Addition in 1 second	1300	60	Room temperature	Stoichiometric amount of NH <sub>4</sub> OH solution

The precipitation temperature, the pH of the initial iron solution and that of the mixture immediately after precipitation, one minute after precipitation and the final pH before the addition of the kerosene and oleic acid and the ferrofluid temperature after heating were recorded.

The saturation magnetisation was measured and magnetisation curves recorded as a response to determine the final quality of the fluid. In order to ensure that the final fluid properties are comparable, the fluids were centrifuged to remove any unpeptized material, large particles and agglomerates and diluted to a density of 0.98 g/cm<sup>3</sup>.

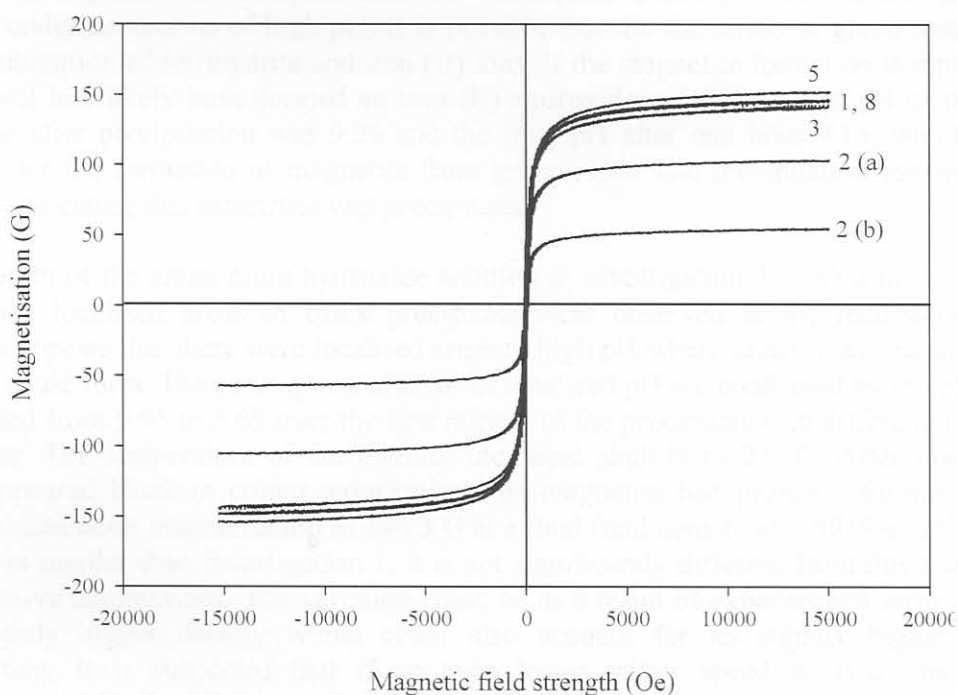
The method of ferrofluid production was as follows:

1. Add 200 ml water to 37.3 g FeSO<sub>4</sub>·7H<sub>2</sub>O.
2. Stir for ten minutes at a speed of 1050 rpm.
3. Add 54 ml FeCl<sub>3</sub>.
4. Rinse out the FeCl<sub>3</sub> container with 220 ml water and add this volume to the iron solution.
5. Stir for an additional eight minutes.
6. Measure pH.
7. Set the required stirrer speed for precipitation.
8. Add required volume of NH<sub>4</sub>OH at the required addition rate.
9. Measure pH immediately after precipitation and again after one minute.
10. Wait the required time delay.
11. Measure final pH.
12. Reduce stirrer speed to 800 rpm.
13. Add 6 ml oleic acid and 38.5 ml kerosene.
14. Heat the mixture over 21 minutes to approximately 80°C (the final temperatures varied but were recorded).
15. Remove from stirrer and allow the mixture to settle and cool on a barium ferrite magnet. The aqueous and organic layers can then be separated.
16. Centrifuge for 30 minutes.
17. Dilute to 0.98 g/cm<sup>3</sup>.

18. Measure the saturation magnetisation.

## 5. RESULTS AND DISCUSSION

Figure 3.2 gives plots of the magnetisation curves for investigations 1, 2, 3, 5 and 8 as outlined in Table 3.2 (curves 1 and 8 lie almost on top of one another) and Table 3.3 gives the temperatures and pH recorded during the investigations.



**Figure 3.2** Plots of magnetisation curves for the investigations

**Table 3.3** Temperatures and pH measured for the various investigations

	Temperature at precipitation (°C)	pH			Temperature of final ferrofluid after heating (°C)	
		Iron solution	At precipitation	After 1 minute		Final pH
<b>1</b>	36	1.32	9.34	9.26	9.13	79
<b>2a</b>	24	1.02	See subsequent discussion		9.21	80
<b>2b</b>	22	1.52	See subsequent discussion		9.18	79
<b>3</b>	27	1.4	Varied from 9.95-5.65		9.4	77
<b>5</b>	34	1.27	9.22	9.15	9.15	79
<b>8</b>	82	1.17	7.49	7.45	8.41	80
<b>9</b>	32	1.06	3.63	4.86	3.95	78



All the magnetisation curves in Figure 3.2 exhibit no hysteresis indicating that the fluids are superparamagnetic.

For investigation 1 where the ammonium hydroxide solution was added rapidly to the iron solutions, a green-black gelatinous viscous mixture was observed immediately. This gelatinous precipitate is then transformed into a black non-viscous crystalline precipitate. The saturation magnetisation of this fluid was 147.6 G at a final fluid density of 0.9853 g/cm<sup>3</sup>. These observations are consistent with a mechanism that describes the formation of magnetite via the formation of a green rust complex and the subsequent decomposition of this complex to magnetite under conditions of high pH. It is possible that the formation of green rusts occurred by the combination of ferrihydrite and iron (II) ions. If the magnetite formation is rapid, the iron (II) ions will less likely have formed an iron (II) hydroxide precipitate. The pH of the mixture one minute after precipitation was 9.26 and the final pH after one hour 9.13, which are ideal conditions for the formation of magnetite from green rusts. The precipitation temperature was 36 °C also indicating that magnetite was precipitated.

Upon addition of the ammonium hydroxide solution in investigation 3, with a low stirrer speed of 130 rpm, localised areas of black precipitate were observed in the reddish-orange iron solution. It appears that there were localised areas of high pH where green rusts and subsequently magnetite could form. The assumption of areas of localised pH are confirmed by the pH readings which varied from 9.95 to 5.65 over the first minute of the precipitation in different areas within the mixture. The temperature of the mixture increased slightly to 27 °C. After one hour, the mixture appeared black in colour, confirming that magnetite had probably formed. The final fluid had a saturation magnetisation of 144.3 G at a final fluid density of 0.9819 g/cm<sup>3</sup>. Although this value is smaller than investigation 1, it is not significantly different from this fluid to make any conclusive assumptions. The variation could be as a result of experimental error and fluid 1 has a slightly higher density which could also account for its slightly higher saturation magnetisation. It is suspected that if an even lower stirrer speed is used, the saturation magnetisation of the final fluid may drop. This will occur if the mixing is so inefficient that areas of the mixture remain at low pH for an extended period of time.

In investigation 5, the ammonium hydroxide solution was added rapidly to the iron solution and the resultant mixture only stirred for one minute before the addition of oleic acid and kerosene. A precipitation temperature of 34 °C was recorded. The same observations as recorded for investigation 1 were observed. The final saturation magnetisation (at 0.9824 g/cm<sup>3</sup>) was 153.6 G.

In investigation 8, the addition of the ammonium hydroxide solution to the iron solution resulted immediately in the precipitation of a black mixture. It is again suspected that the mechanism is the same as for investigations 1 and 5. The final saturation magnetisation was 147.8 G at 0.9802 g/cm<sup>3</sup>.

Investigation 9 did not yield a ferrofluid. No magnetic material was precipitated, instead a mixture of a brown rusty colour was precipitated and the appearance of this mixture remained the same throughout the stirring following precipitation (see Figure 3.3). The precipitate later



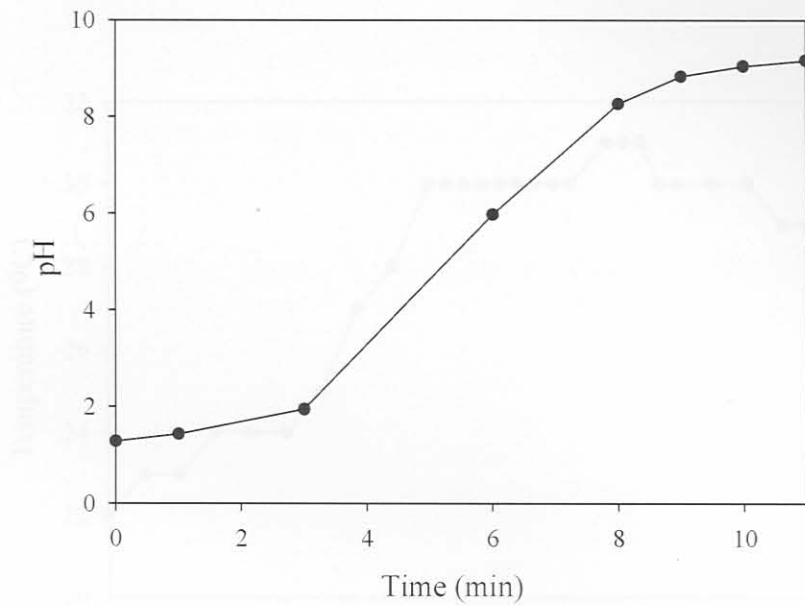
separated into four layers: a layer containing the brown precipitate at the bottom, a greenish aqueous layer in the middle, a layer with brown precipitate and the oleic acid-kerosene mixture at the top. The reason two layers of brown precipitate are observed is probably because a portion of the precipitate contains trapped kerosene molecules which makes it less dense. [28] The pH at precipitation was 3.63 and that after one minute 4.86. The final pH after an hour was 3.95. According to Figure 3.1, it is likely that at these low pHs, goethite could form. Akaganeite is another possible non-magnetic product as the formation of akaganeite is likely in solutions containing chlorides. It is possible that some green rusts formed, but at these low pHs, the green rust would probably have been transformed to goethite or lepidocrocite (assuming a pH of just below 5 would be suitable for this reaction to occur). It is also likely that ferrihydrite formed. The iron (II) ions may have formed insoluble iron (II) hydroxide from which the displacement of the iron (II) ions would be difficult at such a low pH for subsequent reaction with ferrihydrite to form magnetite.



**Figure 3.3** Brown precipitate produced during investigation 9

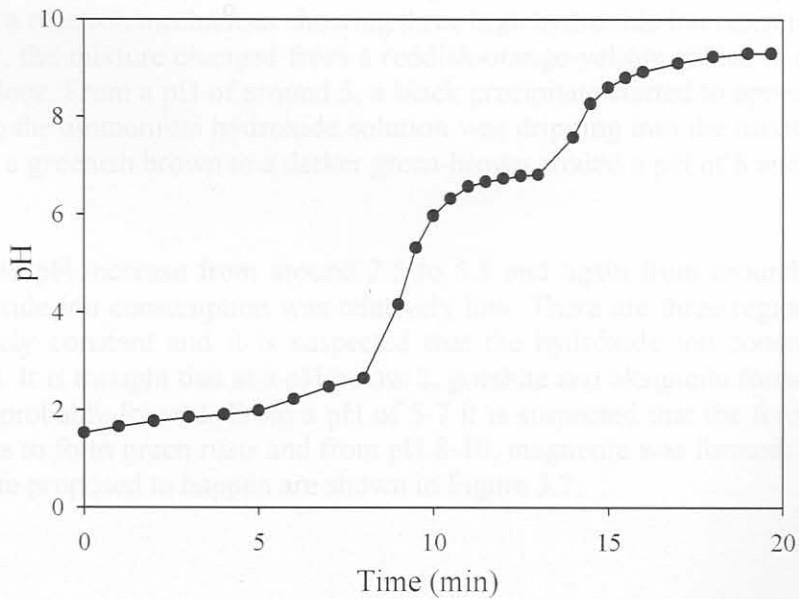
The results from investigation 2 proved to be very interesting. Two of these investigations were performed. In the first investigation, the stirrer speed was not increased from 1050 to 1300 for the precipitation reaction and the investigation was therefore repeated. The results were, however, recorded. This investigation was called 2(a) and the subsequent investigation 2(b). The ammonium hydroxide addition rate in 2(a) was 12 ml/min whilst that for 2(b) was 6.8 ml/min.

In investigation 2(a) it was noted that there was a low pH initially. This pH increased over the course of the ammonium hydroxide solution addition to yield a final pH of 9.17 (Figure 3.4). The temperature also increased to 36 °C.



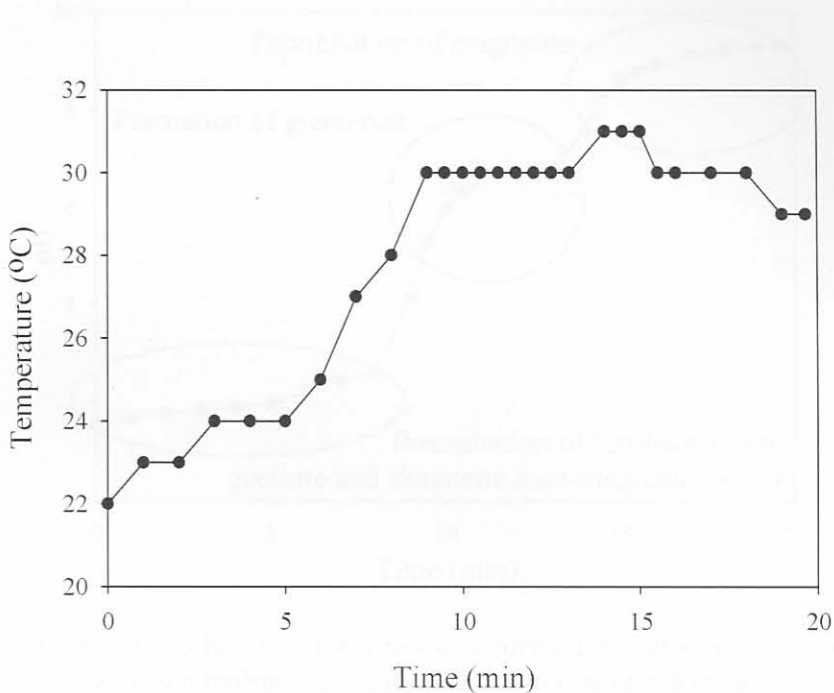
**Figure 3.4** Plot of pH versus time for the ammonium hydroxide solution addition rate of 12 ml/min

When the investigation was repeated, a more detailed recording of the pH was performed. The results are shown in Figure 3.5 with the changes in temperature shown in Figure 3.6.



**Figure 3.5** Plot of pH versus time for the ammonium hydroxide solution addition rate of 6.8 ml/min

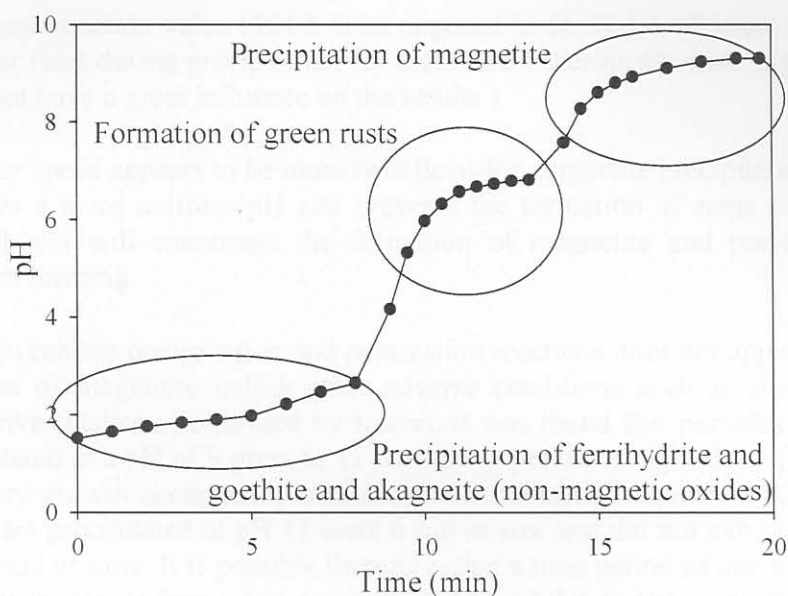




**Figure 3.6** Plot of temperature versus time for the ammonium hydroxide solution addition rate of 6.8 ml/min

The plot of pH versus time shows two distinct regions where there was a rapid change in pH. This is typical of a reaction mechanism showing three high hydroxide ion consumption reactions. At a pH below 2, the mixture changed from a reddish-orange-yellow colour to a darker red and then an ochre colour. From a pH of around 5, a black precipitate started to appear at the walls of the beaker where the ammonium hydroxide solution was dripping into the mixture. The mixture then turned from a greenish brown to a darker green-brown around a pH of 8 and then to a glossy black.

There was a rapid pH increase from around 2.5 to 5.5 and again from around 6.5 to 8 during which the hydroxide ion consumption was relatively low. There are three regions where the pH remained relatively constant and it is suspected that the hydroxide ion consumption in these regions was high. It is thought that at a pH below 2, goethite and akaganeite formed. Above pH 2, ferrihydrite was probably formed. From a pH of 5-7 it is suspected that the ferrihydrites reacted with iron (II) ions to form green rusts and from pH 8-10, magnetite was formed. The areas where these reactions are proposed to happen are shown in Figure 3.7.



**Figure 3.7** Proposed mechanisms for iron oxide formation that were observed with an ammonium hydroxide solution addition rate of 6.8 ml/min

The plot of temperature versus time (Figure 3.6) shows a gradual increase from 22 to 31 °C as the green rust complex forms and magnetite is precipitated. The temperature drops off slightly after 16 minutes and it is believed that the mixture cools slightly while it is being stirred.

The final saturation magnetisations for investigations 2(a) and 2(b) were 104.8 G (0.9827 g/cm<sup>3</sup>) and 56.31 G (0.9836 g/cm<sup>3</sup>) respectively. The magnetisation was low probably because of the formation of non-magnetic material before the magnetite could precipitate.

## 6. CONCLUSIONS AND RECOMMENDATIONS

From the investigations conducted into the preferred conditions for the precipitation of magnetite, the following conclusions can be made:

- It appears that magnetite is produced through the formation of green rusts. The green rusts are produced from ferrihydrites and iron (II) ions. Magnetite is then produced by the dehydroxylation of the green rusts. High pH favours the formation of magnetite.
- Rapid addition of ammonium hydroxide solution is recommended. The rapid addition of the solution raises the pH to the range required for magnetite formation and prevents the formation of non-magnetic products. The rapid formation of green rusts through the use of iron (II) ions prevents the formation of insoluble iron (II) hydroxides which are less available for reaction with ferrihydrites. It was observed that adding the ammonium hydroxide at approximately twice the rate (12 ml/min as opposed to 6.8 ml/min) led to almost double the



saturation magnetisation value (104.8 G as opposed to 56.31 G). (It must be borne in mind that the stirrer rates during precipitation for these two experiments were slightly different but this should not have a great influence on the results.)

- A rapid stirrer speed appears to be more beneficial for magnetite precipitation. A rapid stirrer speed ensures a more uniform pH and prevents the formation of areas of localised pH. A uniform high pH will encourage the formation of magnetite and prevent non-magnetic products from forming.
- The time between the precipitation and peptization reactions does not appear to be critical to the formation of magnetite unless other adverse conditions such as slow stirrer rate are present. In investigations performed by Jolivet, it was found that particles of size 9 nm that were precipitated at a pH of 9 grew to 11 nm over a period of eight days. [29] It is proposed that secondary growth occurred by dissolution-crystallisation equilibria (Ostwald ripening). Those particles precipitated at pH 11 were 6 nm in size and did not exhibit any growth over the same period of time. It is possible therefore, that a time period of one hour was sufficient to ensure that magnetite forms, but not sufficient to exhibit particle growth which could lead to improved magnetic properties. On the other hand, it could be that growth is not significant and the mechanism by which growth occurs does not favour large particle sizes.
- The temperature of the iron solution before precipitation did not appear to be critical in the formation of magnetite. The ammonium hydroxide solution addition rate and stirrer speed to ensure correct pH conditions are thought to be more critical.
- The final pH as a function of volume of ammonium hydroxide added is critical to the formation of magnetite. Sufficient ammonium hydroxide should be added 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.