Improvements in the precipitation of metal ions by magnesium hydroxide.

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Improvements in the Precipitation of Metal Ions by Magnesium Hydroxide.

by

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Abstract

The removal of many metal ions from solution with bases by precipitation and filtration is well known. Due to it's limited solubility, $Mg(OH)_2$ gives many benefits over the other commonly used bases in terms of safety and post-treatment processes such as residual mass and volume. The use of $Mg(OH)_2$ as the base in these reactions, however, does not give satisfactory results in many cases, the levels of metal ions in solution after treatment remaining too high to allow discharge into public waterways. In order to aid these reactions, the use of extra reagents along with the base has been studied. These additives take the form of either donor ligands, e.g. PPh_3, TMEDA, or other metal solutions, typically trivalent metals i.e. Fe^{3+}, Al^{3+} or metal oxides i.e. Fe_2O_3, Al_2O_3.

Following previous studies where P- and N-donor ligands, used in catalytic quantities had shown great increases in the %age of metal ions removed from complicated, multiple metal ion effluent systems, the reactions of individual metal ion solutions with these ligands showed disappointing results. After testing separate solutions of Cu^{2+}, Fe^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+} and Al^{3+}, only Fe^{2+} showed the same improvements seen in the mixed ion systems. Decreases in %age of Cu^{2+} removed were observed for reactions including these ligands .Decreasing removal was seen with increasing ligand addition. This is due to the formation of soluble complexes which are unaffected by the pHs achieved in the reactions. The other metal ions tested showed little change for any addition of these ligand reagents.

Addition of equivalent amounts of an easily precipitated metal ion, i.e. Al^{3+} or Fe^{3+}, to a more difficult to treat metal ion solution, i.e. Ni^{2+} or Zn^{2+}, gave large improvements on the removal of the ions by treatment with $Mg(OH)_2$. Tenfold increases in removal of the ions were seen in the reactions, allowing dischargable concentrations to be achieved in far lower times than previously obtained. Addition of the M(III) solutions, while improving the metal ion removal, increased the amount of $Mg(OH)_2$ required for treatment. An industrially available additive, containing Al and Fe sulphates, was tested in a similar fashion giving the same beneficial results. The use of identical amounts of base, with and without this additive showed that improvements in removal of metal ions were obtained even over increasing the relative amount of base added. To overcome this problem, the M(III) species were added in the form of oxides, e.g. Al_2O_3. This removed the need for extra base but the results were disappointing compared to the addition of the M(III) ions as solutions, only ~10% increase in precipitation with a tenfold addition of oxide.

None of these reactions achieved the $Mg(OH)_2$ buffer pH of 10.5 even when large excesses were added. This has been attributed to coating of the solid $Mg(OH)_2$ particles by precipitating M(II) hydroxides which prevented dissolution and kept the majority of the hydroxide from taking part in the reaction. The addition of the extra M(III) species provided preferential sites for the M(II) hydroxides to form on and thus allowed the reaction of all of the $Mg(OH)_2$ added.

The use of ultrasound to improve these reactions, both instead of and as well as the use of additives, was studied and was seen to give further improvement in these reactions. The ultrasound not only provided an increase in the energy of the systems through a general heating of the solution, but the physical forces created aided the break-up of both the solid $Mg(OH)_2$ particles and any coatings that may have built up on them. The use of a 16kHz ultrasound probe produced large improvements in the removal of metal ions and when used in conjunction with M(III) additives dischargable concentrations were achieved in only 30 minutes.

Through the use of various additives and conditions, $Mg(OH)_2$ has been shown to be a viable option in the effluent treatment industry.

The reactions were performed mainly on laboratory prepared solutions of the relevant metal ions, with commercially available $Mg(OH)_2$ suspensions. The results were obtained from observation of the pH of the reaction mixtures and concentrations of the metal ions remaining in solution after filtration, determined by atomic absorption spectrophotometry.

To my Mam and Dad

Declaration.

The work described in this thesis was carried out in the University of Durham between October 1994 and September 1997. This work has not been submitted, either completely or in part, for a degree in this or any other University and is the original work of the author except where acknowledged by reference.

Statement of Copyright.

"An infinite number of monkeys,
given an infinite amount of time
and an infinite number of typewriters
will eventually produce the complete works of Shakespeare."

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The New Inn	for salvation
Grad. Soc. A.F.C.	for giving me something, and someone, to kick

Abbreviations.

ppm = parts per million ≡ mg l^{-1}

TMEDA = N,N,N',N'-tetramethylethylenediamine

bipy = 2,2'-bipyridine

dppe = 1,2-bis(diphenylphosphino)ethane

py = pyridine

en = ethylenediamine

X^- = halide ion

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Chapter 1

Introduction

1. Introduction.

1.1 Background.

Many industrial processes involve stages that require large quantities of water. These stages are typically washings, coolings and similar. The water for these processes often dictates the location of the industrial site, and is most commonly taken directly from public water sources, such as rivers, lakes, reservoirs or the sea. The waters used in these processes can react with some of the species involved, leaving large concentrations of hazardous materials in the water. The use of these large quantities of water requires that they be disposed of speedily after use. Simply discharging these solutions back into the water sources from which they were drawn is simply not an option if they contain high levels of hazardous materials. These solutions require treatment before discharge is allowed.

There are many sorts of species that can contaminate these water processes and must be removed. These include

- Metals, e.g. Fe^{2+}, Ni^{2+}, Al^{3+};
- Organic substrates, solvents;
- Polymers;
- Inorganic ligands, e.g. phosphates, sulphates.

Treatment for these contaminants may take many different forms, for example:

- Alkali addition;
- Complexation;
- Electrochemical.

The use of alkalis in the treatment of effluents discharged by many industrial processes is well known [1]. They have been used in purification processes for a long time, due to their simplicity and low expense.

This project has concentrated on the treatment of effluents containing high concentrations of metal ions. Excess concentrations of some metals ions can cause diseases such as anaemia (iron), liver cirrhosis (iron and copper), and Alzheimer's Disease (aluminium) to name but a few [2,3]. Metal ion discharge concentrations are negotiated with local authorities; values agreed on are usually in the order of 1ppm, and a typical set of limits is shown in **Table 1.1**[4,5].

Table 1.1

Metal	**Discharge Limit /ppm**
Fe	0.5
Cu	0.5
Ni	1
Zn	1
Pb	1
Cr	1

There are various ways of tackling this problem. Each method hinges on chemical reaction of the metal species which enables the pollutant to be removed by physical means. Application of a current can reduce metal ions to their neutral metallic form which can easily be removed by filtration [6]. This is a very expensive process and as such is not used commercially. It is more commonly used to remove metal ions from ground deposits.

The addition of a chelating agent to the solutions and the formation of complexes is another method. The ligands added take the form of large organic molecules such as cryptands, spherands and polymeric species. These additives can be tailored to target only specific metal ions, often by the manipulation of the size of the donating site [7]. Again this process is expensive, requiring large quantities of ligand to be added in order to remove the metal ions to low enough concentrations.

The most commonly used technique is the treatment of the solutions with base to raise the pH of the system to such a level that the metal ions are no longer soluble, and precipitate out as metal hydroxides or hydrated oxide species. Each metal ion has a characteristic solubility product, K_{SP}, at which this precipitation process occurs, **Table 1.2** [8,9].

$$M^{n+}{}_{(aq)} + nOH^{-}{}_{(aq)} \overset{K_{SP}}{\rightleftharpoons} M(OH)_{n(s)}$$

Equation 1.1

$$K_{SP} = \frac{[M^{n+}{}_{(aq)}][OH^{-}{}_{(aq)}]^{n}}{[M(OH)_{n\,(s)}]}$$

Equation 1.2

The concentration of a solid is defined as 1, therefore

$$K_{SP} = [M^{n+}{}_{(aq)}][OH^{-}{}_{(aq)}]^{n}$$

Equation 1.3

As the concentration of OH^- increases the overall ionic product increases. This can continue until the solubility product is reached. At this point, in order to retain an equilibrium, the concentration of M^{n+} decreases. This occurs as the precipitation of M hydroxide, $M(OH)_n$.

Table 1.2

Metal Hydroxide	**K_{SP}**‡	**pK_{SP}**
$Mg(OH)_2$	1.1×10^{-11}	10.96
$Mn(OH)_2$	2.0×10^{-13}	12.70
$Cd(OH)_2$	2.0×10^{-14}	13.70
$Pb(OH)_2$	4.2×10^{-15}	14.38
$Fe(OH)_2$	7.9×10^{-16}	15.10
$Zn(OH)_2$	2.0×10^{-17}	16.70
$Ni(OH)_2$	6.5×10^{-18}	17.19
$Cu(OH)_2$	1.6×10^{-19}	18.80
$Cr(OH)_3$	6.7×10^{-31}	30.17
$Al(OH)_3$	1.0×10^{-33}	33.00
$Fe(OH)_3$	2.0×10^{-39}	38.70

Traditionally this sort of environmental control most commonly used alkalis such as NaOH, Na_2CO_3 or $CaCO_3$ to increase the pH of the system. The sodium salts are widely used and are very effective at this process. There are several drawbacks to their use in this way, however, **section 1.2**. The calcium salts are used in large quantities mainly due to their high availabilities.

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‡ K_{SP} has dimensions of $mol^{n+1}dm^{-3(n+1)}$ where the hydroxide is $M(OH)_n$.

1.2 Neutramag

In recent years $Mg(OH)_2$ has emerged as a viable alternative in the treatment of effluents containing high concentrations of metal ions and acidity. Britmag Ltd. (formally Redland Minerals), a company based in the north east of England, has looked at the use of $Mg(OH)_2$ in this field. Britmag produces $Mg(OH)_2$ in different grades for many different processes.

- Treatment of gas flues;
- Neutralisation of acids;
- pH correction for potable and process water;
- Additive in light fuel oil for improvement in boilers;
- Treatment of metal rich effluents.

The magnesium hydroxide can easily be produced by roasting the ore dolomite, $MgCa(CO_3)_2$, and washing the oxide produced with sea-water, **Equation** . The magnesium salts present in the sea-water react with the magnesium oxide producing magnesium hydroxide. The magnesium hydroxide is much less soluble than the calcium salts present and precipitates out, leaving the calcium salts in solution, **Equation** . The solid $Mg(OH)_2$ is then allowed to settle to the bottom of the reaction tanks. This slurry is then removed from the bottom of the tank where the concentration of calcium salts is very low.

$$MgCa(CO_3)_2 \xrightarrow{-2CO_2} CaO.MgO$$

Equation 1.4

$$CaO.MgO + MgCl_2 + 2H_2O \longrightarrow 2Mg(OH)_2 + Ca^{2+} + 2Cl^-$$

Dolime + Magnesium salts in sea-water

Neutramag + Spent calcium salts in sea-water

Equation 1.5

This slurry is then washed again with either more sea-water or fresh water, giving two different grades, Neutramag S and F respectively. The Neutramag F is more expensive as it requires fresh water at this stage, which must be piped in and paid for rather than pumped from the sea. It is only used therefore in cases when the concentration of sodium or chloride ions needs to be controlled. Other than that there is no difference between the two grades.

1.3 Advantages of Neutramag.

Magnesium hydroxide is only sparing soluble, its K_{SP} is only 1.1×10^{-11} mol^3dm^{-9}, c.f. K_{SP} of $Ca(OH)_2 = 5.5\times10^{-6}$ mol^3dm^{-9} [8]. It is this lower solubility that gives Neutramag its advantages over traditional bases.

Safety	The low solubility of Neutramag means that even when present in large excess, the pH of the solution will never be higher than approximately 10.5, **Figure 1.1**, which means redissolution of metal ions is much less likely. This also means that the system is much safer and requires that less strict health and safety regulations need be applied. $Mg(OH)_2$ suspensions are so innocuous that they are used in a pharmaceutical grade as remedies for acid indigestion. NaOH and $CaCO_3$ react vigorously with water and produce a great deal of heat, which again requires higher levels of monitoring and safety precautions to be used. As Neutramag is present as a suspension already, there are no problems in this respect. The lower maximum pH also means that overdosing the system so that a large quantity of unreacted Neutramag is discharged is not damaging to the environment.

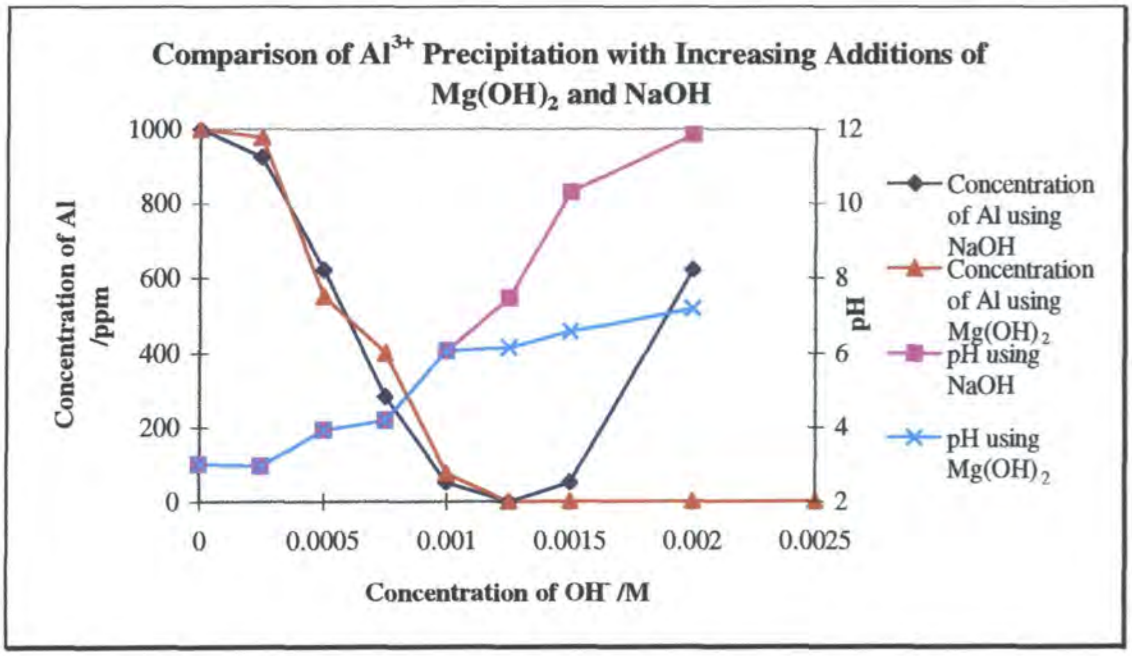


Figure 1.1

Physical Properties. Neutramag has benefits from its physical properties that are not insignificant on an industrial scale. Its low solubility means that it does not freeze above 0°C c.f. 47% NaOH, which is the usual concentration used for these processes, which freezes at 8°C. (Slight variations in concentration, above or below the 47% figure, increase the temperature of freezing even further [9].) This lower freezing temperature reduces the need for heated storage tanks and insulated pipework. No difficulties with release of heat on mixing with the aqueous effluent solution are experienced, as noted above. With the use of correct pumps and valves, the Neutramag slurry can be treated in the same way as a solution so there is no drawback in using it with respect to having to refit the existing pipelines.

Sludge volumes

The lower solubility of $Mg(OH)_2$ means that the precipitation proceeds more slowly. This is due to the solid $Mg(OH)_2$ needing to dissolve before the reaction can continue. This longer reaction time means that the particles precipitated form larger aggregates. These larger particles are much easier to drain and dry than their sodium or calcium base induced counterparts and hence leave much lower residual sludge volumes [10,11]. These lower volumes are also achieved much more quickly than is found with the Na or Ca salts, as illustrated in **Figure 1.2**.

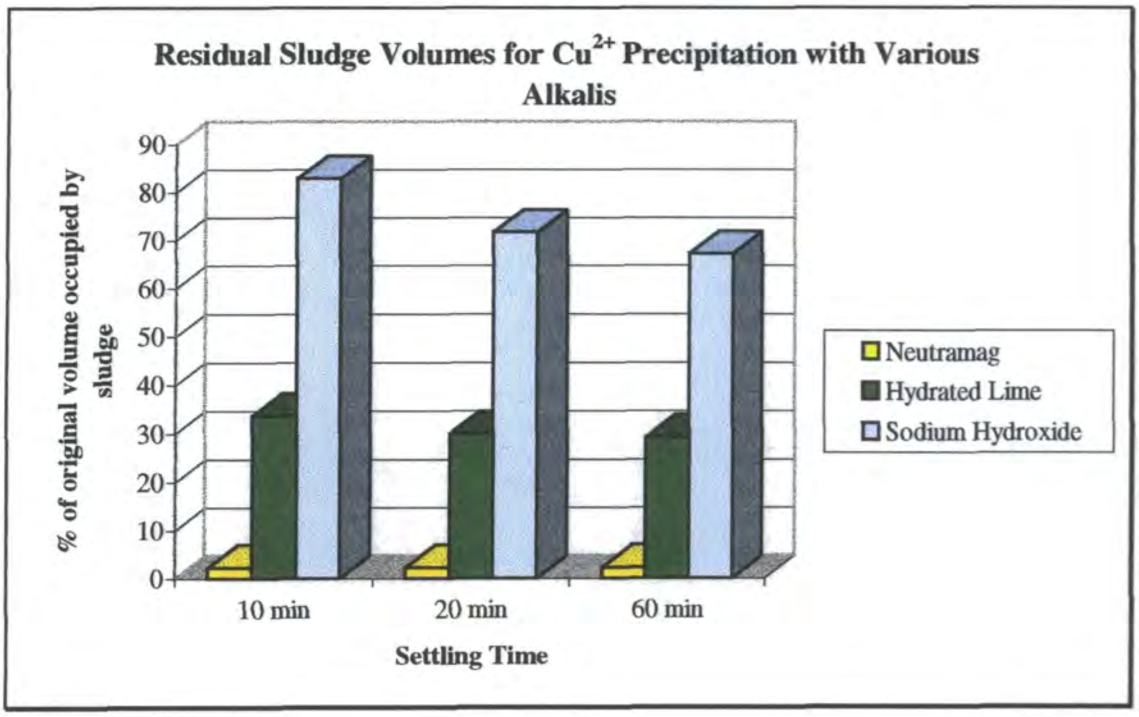


Figure 1.2

The residues of precipitated metal hydroxides must be removed from the site and disposed of. This is most often done by removal to landfill sites. The lower volumes achieved with Neutramag mean that more waste can be transported per shipment (fewer journeys) and more waste can be disposed of in the volume of landfill available. As landfill is taxed by mass, removal of more of the water from the residue will reduce the mass and therefore the cost of disposal.

1.4 Previous Work.

The vast majority of the research in this field has been done by Richard Foreman [9], in a report on the initial uses of Neutramag, and Mark Roden [12], in a single year project on improving the reactions. This second project was a direct precursor to the present studies.

Initial studies on the use of Neutramag were as an acid neutralising agent. Although the pH increases at a slower rate than with NaOH or lime, this was not an indication of slower reaction. Studying the pH of the solution, which gave the concentration of $H^+_{(aq)}$ at a given time and hence the fractional removal of acidity, allowed us to see that the acidity had been largely removed, **Figure 1.3**. Although the pH was still less than 4, due to the logarithmic nature of the scale used, virtually all of the acid had been removed. The pH required a longer time to get up to its natural buffer value of approximately pH 10 as the solid $Mg(OH)_2$ needed time to dissolve. This is not the case with the more soluble NaOH and the pH is increased almost immediately to that of the buffer region.

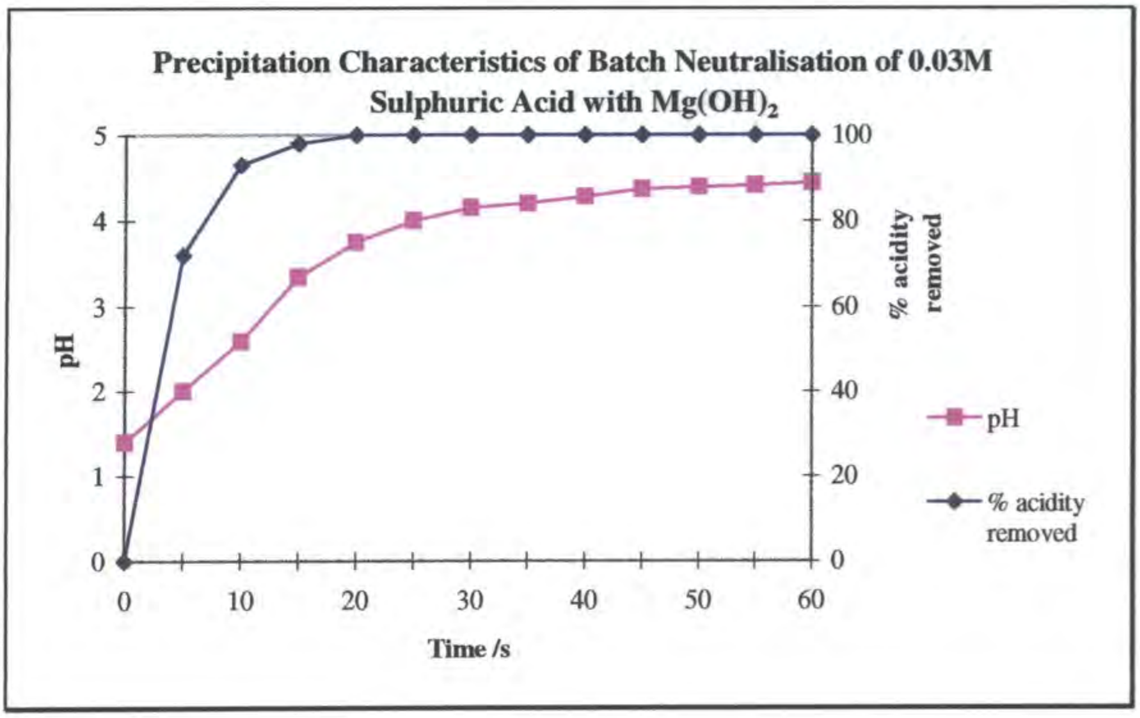


Figure 1.3

The study then moved on to the use of Neutramag to precipitate metal ions from solution. The primary reactions in this area looked at the percentage removal of single metal ions from solutions using Neutramag to raise the pH to 7. In general, metal hydroxides with pK_{SP}s above 18 could be easily precipitated in this way, giving 100% removal, **Table 1.2** and **Figure 1.4**. Metal hydroxides with pK_{SP}s below 18 did not completely precipitate, **Figure 1.5**, although the use of excesses of Neutramag was seen to aid these reactions.

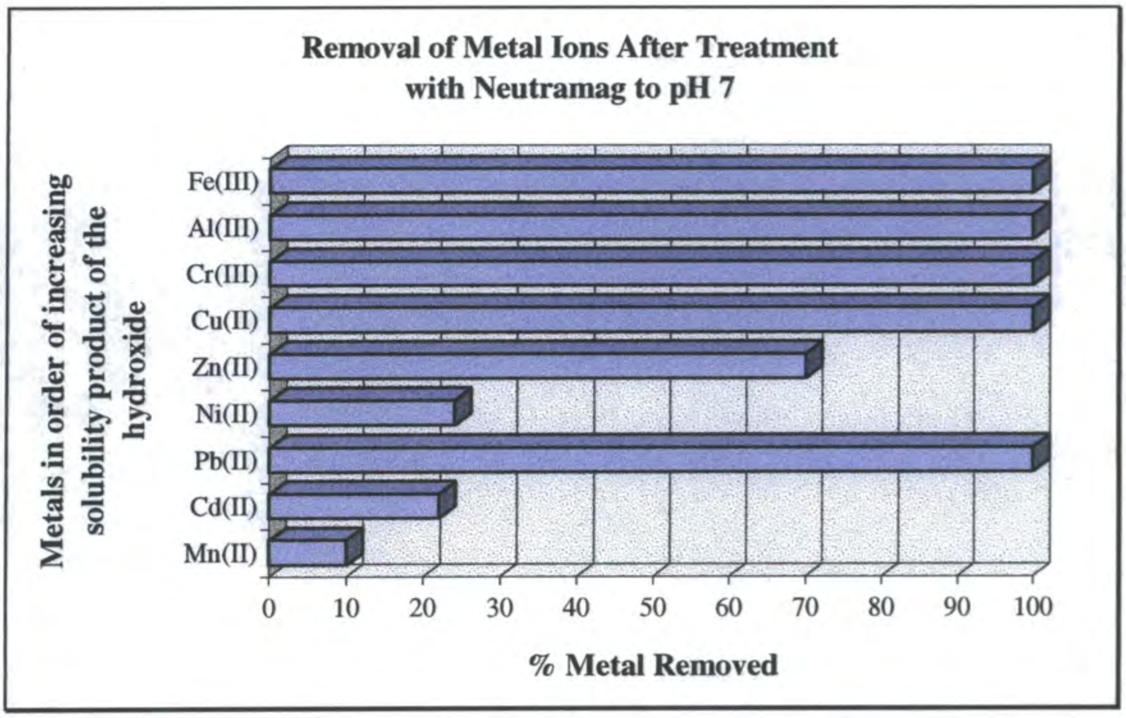


Figure 1.4

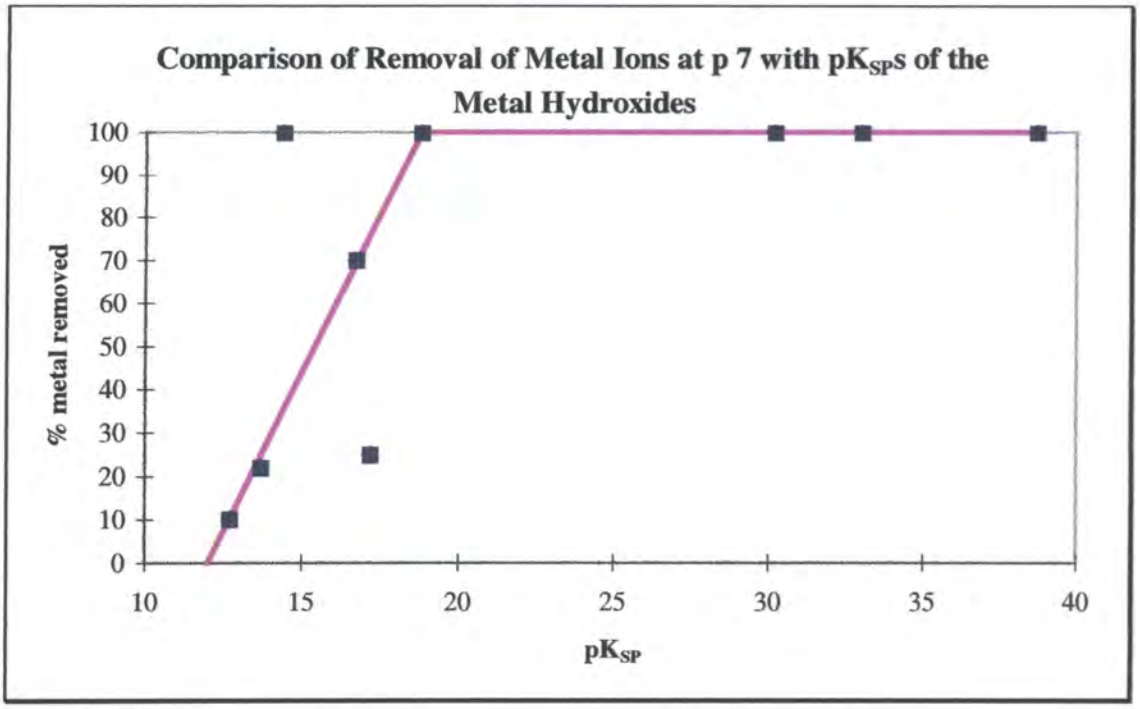


Figure 1.5

Treatment of a metal from each side of this pK_{SP} value of 18, Cr(III) and Zn(II), with differing stoichiometric ratios of Neutramag showed differing results, **Figure 1.6** and **Figure 1.7**. These reactions were allowed to go to completion each time.

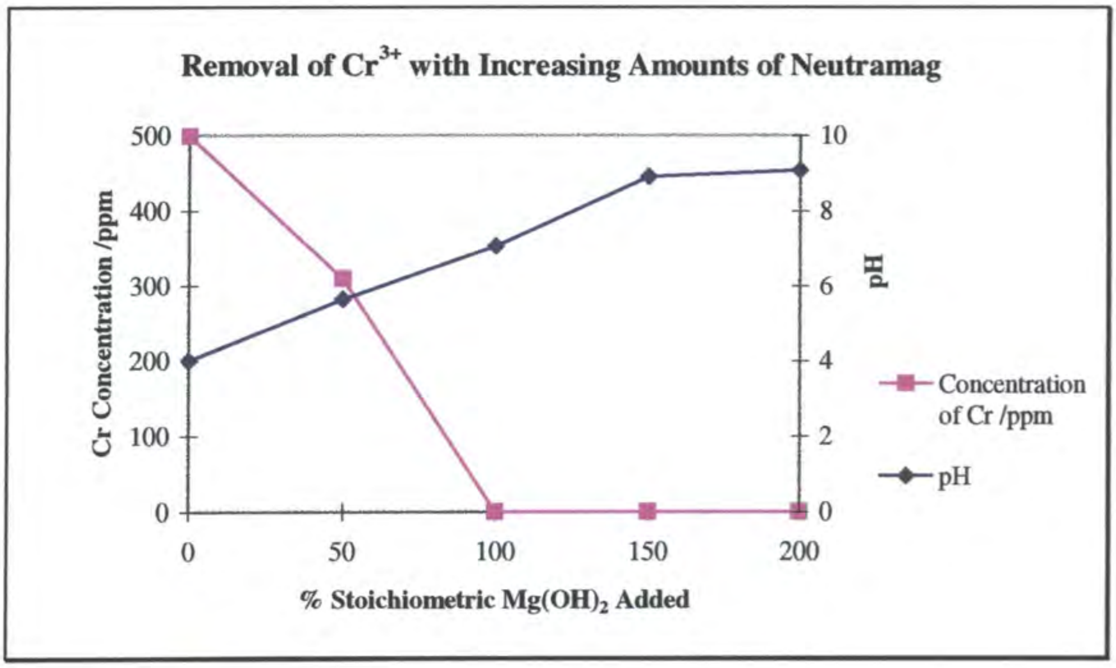


Figure 1.6

The easily precipitated Cr^{3+} gave 100% removal in a 1:1 reaction even though the pH was only 7. Adding further Neutramag to this system only increased the final pH.

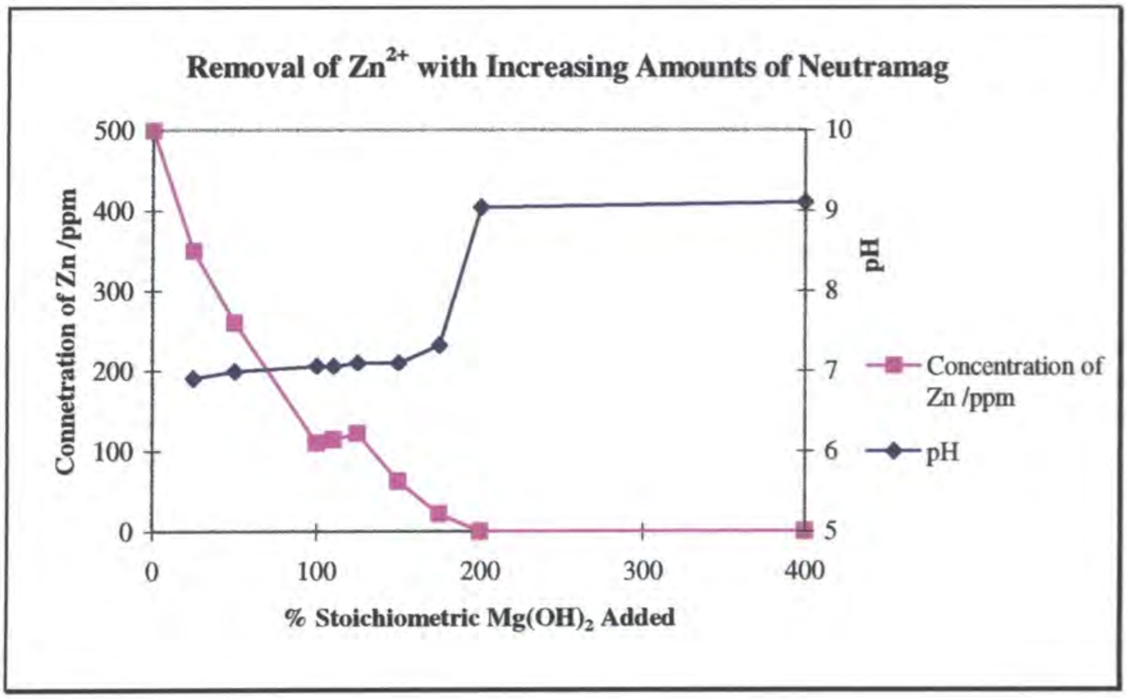


Figure 1.7

In the reaction with the more soluble Zn^{2+}, adding a 1:1 ratio of Neutramag only achieved an approximately 80% removal. Adding further Neutramag to this system slowly increased the % precipitated, although the final pH achieved did not increase notably until the metal ion removal reached 100%, at a 2:1 ratio.

The previous project [12] carried on from this point, concentrating initially on the more commonly found, difficult to precipitate, Ni^{2+} and Zn^{2+} ions.

In these reactions, treatment of Zn^{2+} showed that removals of above 10% and pHs higher than ~7.1 were very hard to achieve. Adding the Zn^{2+} solution to a Neutramag suspension showed that the reaction proceeded up to a certain point and then stopped completely. Even the use of a 5:1 excess of Neutramag obtained only a 60% metal ion removal after 2 hours.

Adding small aliquots of Zn^{2+} solution over time to the Neutramag suspension removed nearly all of the metal from solution (98%) using a 10:1 excess of Neutramag. Addition of further Zn^{2+} solution, to a ratio of 2:1, Neutramag:$Zn^{(II)}$, showed that, if left, good removal was possible using lower excesses of Neutramag, 98% again being removed after 2 days. A similar reaction performed using Ni^{2+} solution gave a 48% removal after 2 weeks. From this it became obvious that nickel reactions would need some kind of extra boost.

The heating of the Neutramag suspension, either directly or through addition to hot metal ion solutions would be beneficial to the precipitation process in several ways.

Increasing the temperature of the reaction by 10°C roughly doubles the reaction rate. The various factors in the Arrhenius Equation, **Equation 1.6**, which dictate this are reasonably close for these reactions and so this generalisation can be made.

$$k = Ae^{\frac{-E_a}{RT}}$$

Equation 1.6

Several reactions were heated by the addition of near-boiling water. Using this method all the zinc was removed at 1.8:1 (80% excess of Neutramag) in less than 2 hours. The nickel reaction also showed great improvement, giving a metal ion removal of greater than 90% precipitated in 2 hours.

Next, the two metal solutions were mixed together and then reacted. At a 1:1 stoichiometric equivalent only 49% of the zinc and 6% of the nickel was removed. As zinc hydroxide has a lower solubility product it was expected to precipitate preferentially, but as only 25% of the metals had precipitated there would be a lot of unreacted Neutramag left in solution. Even if there were no further reaction, the unreacted Neutramag should have dissolved and the pH risen to approximately 10.

Repeating the reaction using varying ratios of the two metals showed that as the relative amount of nickel in the solution increased, the % removal of both metal hydroxides precipitated fell, nickel precipitation falling more rapidly than zinc, **Figure 1.8**.

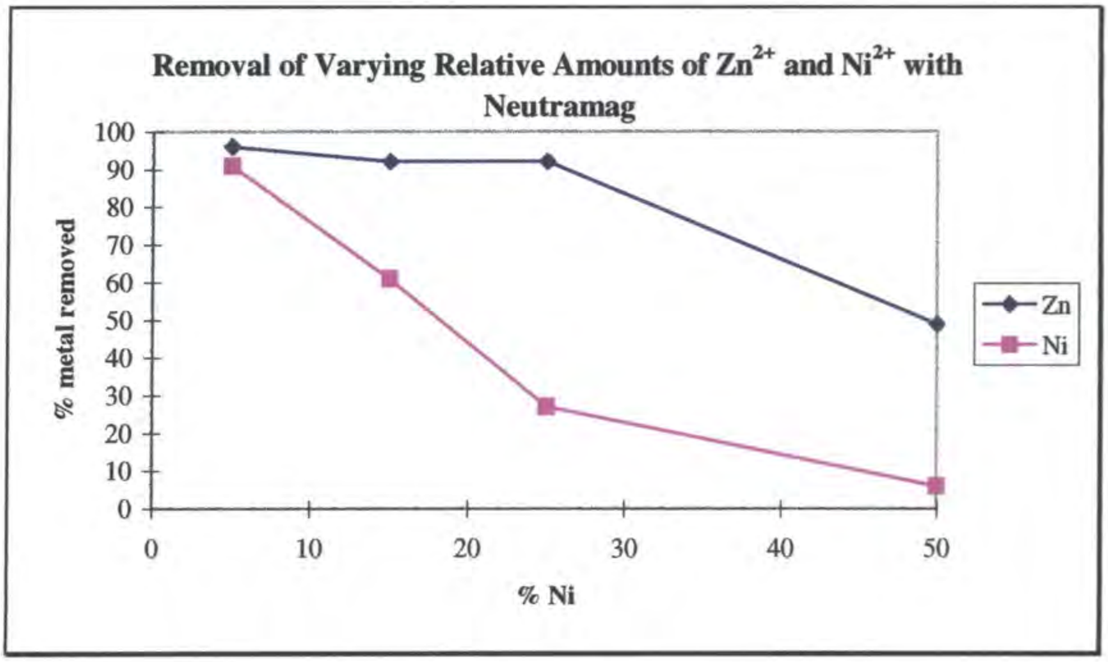


Figure 1.8

In order to precipitate the metal ions, the concentration of OH^- ions must be increased, **section 1.1**. Simply adding more Neutramag had been shown to be ineffective, so other methods of increasing the pH were tried. To this end the addition of alkaline buffers was looked at. The buffers tried were acetates. Addition of a metal acetate to the already acidic solutions would generate acetic acid, thus completing the buffer system.

To minimise the possible variables in the system, magnesium acetate was added; this avoided the introduction of different cations. Using the buffer gave much better results for both zinc and nickel in less than two hours. Other acetates were also tried, but the only significant advance was found for ammonium acetate, **Figure 1.9**.

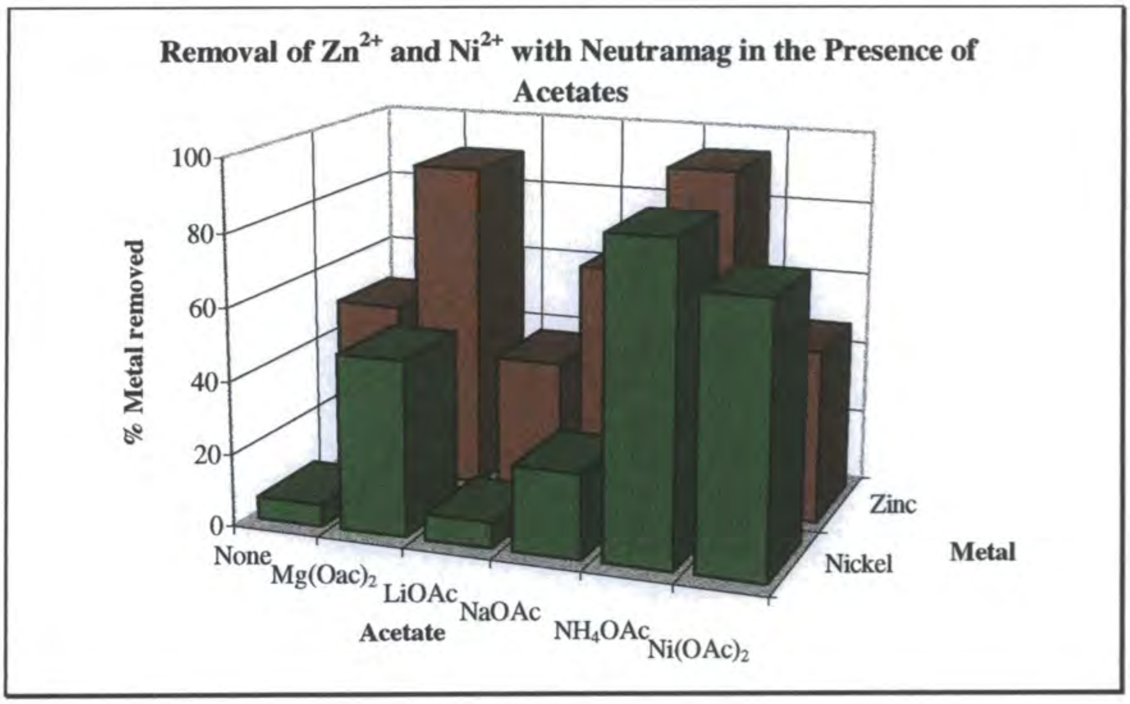


Figure 1.9

The two acetates, magnesium and ammonia, were then used together in reactions at differing ratios. Although no particular mixture ratio of the two acetates stood out as being better, it was seen that the more acetate that was added to the solution, the greater the effect on the rate of reaction.

It was unclear at this point whether it was the cations (Mg^{2+}, NH_4^+) or the anions ($CH_3CO_2^-$) that were affecting the reaction. To test for this, magnesium and ammonium nitrates were added instead of the acetates. This gave very good results, removing all the zinc and 96% of the nickel. Increasing the concentration of magnesium ions in solution would have decreased the solubility of the Neutramag, (from $K_{SP} = [Mg^{2+}][OH^-]^2$), **Equations 1.1 - 1.3**, so ammonium nitrate was added on its own in a repeat reaction. This reaction gave comparable results (100% zinc removed; 91% nickel removed), with much less ammonium species added, **Figure 1.10**.

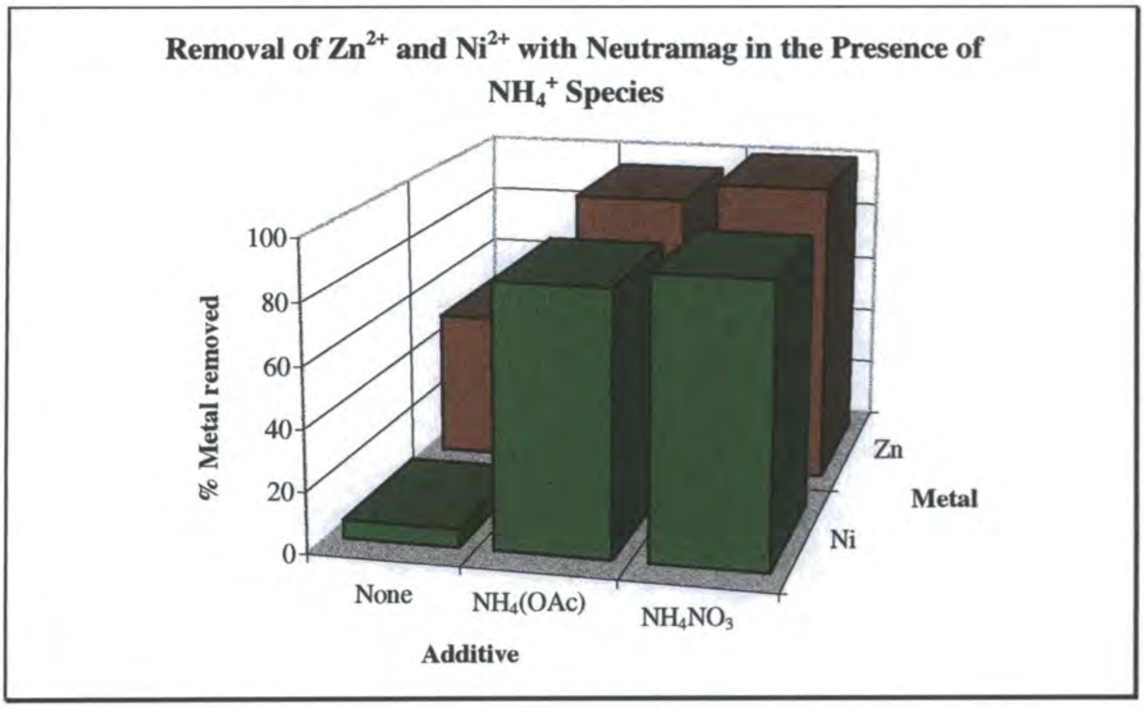


Figure 1.10

The method of heating the reaction was altered at this point. Instead of heating the metal solution, the Neutramag suspension was heated to approximately 60°C before addition to the room temperature metal solution. The volume of Neutramag suspension used in these reactions was a lot smaller than that of the metal solutions, and so it was more efficient to heat the smaller quantity. This method did not prove to be as effective as heating the metal solution. The drop in reactivity was probably due to the lower average temperature of the mixed reactants.

Ammonium chloride was tested next using both heated and room temperature Neutramag suspensions. The heated Neutramag gave 98% Zn; 89% Ni removal in three hours and the room temperature reaction gave 98% Zn; 92% Ni removal in 48 hours. This in itself had brought the reaction time down by a factor of 10 from what Britmag had achieved. The common factor in these reactions was the addition of a NH_4^+ species. This seemed to indicate that addition of these ammonium ions was affecting the reaction kinetics. It was thought that a new reaction pathway was being made available.

An interesting point noticed here was that far more metal ions were being precipitated, compared to reactions without the ligands, than the amount of ligand being added. This seemed to indicate some sort of catalytic reaction was taking place.

Many metals ions, $[M(H_2O)_x]^{n+}$, in the presence of concentrated ammonia, will produce metal ammine complexes, $[M(H_2O)_x(NH_3)_y]^{n+}$. Less concentrated solutions give less substituted complexes, i.e. smaller values of y. It seemed feasible therefore that if there was any ammonia present in the solution, some complexation was occurring. As the reactions proceeded, the pH increased to alkalinity, where the ammonium cations would be deprotonated leaving free ammonia, **Scheme 1.1**. The ammonia would then be free to go on to complex with the metal ions.

$$NH^{4+} + OH^- \rightleftharpoons NH_3 + H_2O$$

$$[M(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [M(H_2O)_5NH_3]^{2+} + H_2O$$

Scheme 1.1 Reaction of Ammonium Ions with Metal Ions in Basic Solutions

If the ammonia was complexing with the metal centres, it seemed likely that other ligands that donate electrons through nitrogen would also affect the reaction. Some common examples of these donors are :- 2, 2' bipyridine (bipy), 1,10 phenanthroline (phen) and thiocyanate (←:NCS$^-$). At this point the spectrochemical series was considered.

The spectrochemical series is a ligand series that is approximately constant for all $M^{(II)}$ ions [13,14]. It displays the increasing metal-ligand bond strength from increasing electrostatic field strengths felt by the d-electrons of the metal. The further up the series, the stronger the bonds and the larger the formation constant of the complex made, **Figure 1.11**.

$X^- < H_2O < RCOO^- < \leftarrow:NCS^- < py < NH_3 < TMEDA < en < bipy < phen < PPh_3 <$

$DPPE < NO_2^- < CN^-$

(X^- = halide: py = pyridine; TMEDA = N,N,N',N'-tetramethylethylenediamine; en = ethylenediamine; bipy = 2,2'-bipyridine; phen = 1,10-phenanthroline)

Figure 1.11 The Spectrochemical Series

It can been seen that the series follows the general progression that, for uncharged ligands, phosphorus donors are better than nitrogen donors which in turn are better than oxygen donors, **Figure 1.12**.

O donors < N donors < P donors

Figure 1.12 General Trend of the Spectrochemical Series

This follows if both ammonia and acetate are acting as donor ligands. In general the stronger the donor ligand, the faster the reaction and it was seen that the presence of ammonia made the reactions work better than with just the acetate. If ligands were to be used in these reactions, the most effective ligand must be identified. Very strong donors such as CN^- would not be desirable. Although CN^- would bind very strongly, it is unlikely to be removed from the metal again by the reaction with OH^-. (CN^- was further limited in these reactions by its toxicity and so was unsuitable to be used in the treatment in this way.) This would not help in the overall reaction if the ligands act in a catalytic manner as thought. There would be a cut-off point where the M-L bond is as strong as possible while the hydroxides can still remove the ligand from the metal.

Instead of trying to raise the pH, the ligands were used in an attempt to form complexes with the metals and aid the reaction by allowing new reaction pathways.

The first of the new ligands to be tried was sodium thiocyanate, another nitrogen donor. This also gave good results 100% Zn and 89% Ni removed in 12 hours with the addition of hot Neutramag. TMEDA (N,N,N',N'-tetramethylethylenediamine) was tried next, **Figure 1.13**. This is a chelating ligand, having two donor sites on each molecule.

Reactions using M:L ratios starting at 10:1 and going down to 2:1 were carried out. These results showed that as the relative amount of ligand increased, so did the rate.

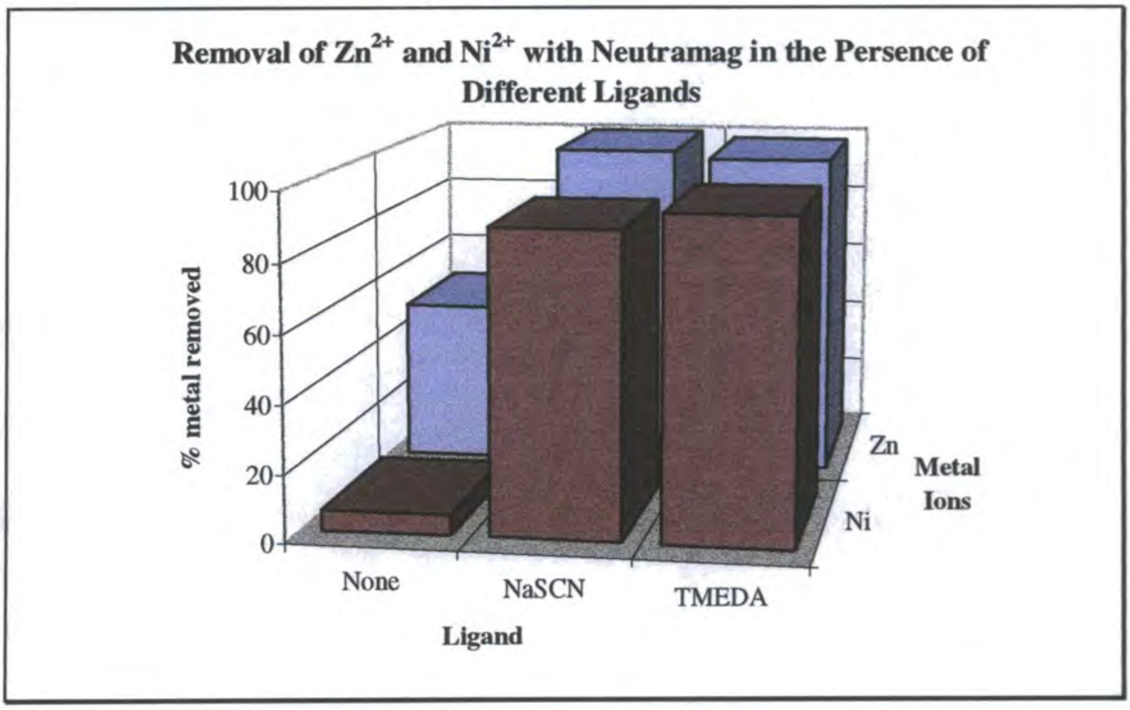


Figure 1.13

It was decided then to move onto more complex solutions with varying metal ions present. These types of solutions were more commonly found in effluents Britmag were asked to treat. The results found in the single metal systems were applied to these solutions.

The first solution studied had high concentrations of iron(II) and nickel. This solution was reacted with many different ligands to see which gave the best results. The ligands tried were NH_4Cl, TMEDA, bipy, phen, NEt_3, PPh_3 and $P(O)Ph_3$.

At that time most river authorities required effluent discharges to be less than 10ppm (1 part per million ≡ 1mg per litre) for each metal ion, the target was to get down to 0.1 ppm, due to dilution of the limited starting effluent sample. At such low concentrations there would be a large scope for errors, but in the comparison of similar reactions most of these should cancel each other out.

It was soon seen that PPh_3 was by far the best ligand for the solution, even in room temperature reactions, removing all the metals down to below the desired concentrations.

This again followed the spectrochemical series, P donors being better than N donors. The reaction was repeated at full strength and again all the metals were removed to well below the discharge limits (down to 0.1ppm c.f. 10ppm).

One thing noticed in these reactions was that the residue filtered off was brown in colour, as opposed to the green colour of iron(II) hydroxide which was expected. This indicated that some oxidation of the iron was occurring in the reaction. Iron(III) is much easier to precipitate than iron(II), K_{SP} of $Fe^{(II)} = 7.9\times10^{-16}$ mol^2dm^{-6}, K_{SP} of $Fe^{(III)} = 2.0\times10^{-39} mol^3dm^{-9}$ [8].

Another industrial sample was tested, this time with high concentrations of iron(II) and titanium. Titanium has its own problems in determining the concentration by atomic absorption, **section 2.3.1**. Using PPh_3 at a metal:ligand ratio of approximately 100:1, virtually all the iron was removed and as much of the titanium as could be detected (<5ppm remaining).

A sample containing a large amount of nickel was the next to be studied. This solution had a very low pH (~1.6) and extra Neutramag was needed to be added to neutralise the excess acid. This acidity led to problems in the accuracy of the aliquots of Neutramag. The amount of Neutramag needed to neutralise the acid was approximately 40× that required to precipitate the metal ions. With these relative amounts, small inaccuracies in the volumes of Neutramag added could mean large variations in the excesses required for precipitation. The solution was diluted and reacted, giving >99% removal of the nickel in 90 minutes using PPh_3.

Increasing the concentration of metal ions in the test solution decreased the relative error (a 1ml error where only 1ml is needed to precipitate the metal is a 100% error, whereas a 1ml error when 20ml is needed is only a 5% error). These reactions showed that in order to precipitate significant amounts of nickel (down to <10ppm) the pH must reach 8.3. As the concentration increased the time needed for the reaction to go to completion increased.

A solution with high concentrations of iron(II) and nickel ions was the fourth industrial sample tested. Only when the solution was reacted for 2½ days did the concentration of iron(II) fall beneath 10ppm. Repeating the reaction with more dilute samples showed that as the concentration doubled, the time required for reaction increased by a factor of 4. A stage process was tried with this solution, adding small aliquots of Neutramag at a time and allowing them to react completely before adding more. This did not show any new information and was a lot more time-intensive.

As there were only limited quantities of industrial effluents available, solutions of metals were prepared and used instead.

The first of these was mainly iron(II) with some nickel and zinc. This solution was reacted with PPh_3 as normal but also had air being bubbled through the solution to aid both mixing and oxidation of $Fe^{(II)}$ to $Fe^{(III)}$. Iron(III) is much easier to precipitate than iron(II) and Redland had had some success using aeration. It was seen that doubling the concentration increased the reaction time by a factor of 2.

There was a definite improvement in the precipitation reactions that far exceeded the amounts of ligand being added. Various ideas were looked at to try to account for the observed results.

When the PPh_3 solution is added to the aqueous solution, the solid PPh_3 is precipitated as it is insoluble in water. The reaction with the metal must therefore be a direct interaction between the aquo-complex and the solid ligand. If the ligand could be dissolved these problems would be minimised and the reaction might work even better.

In order to get the ligands into solution, and so hopefully improve the reactivity with the metal ions, some modifications would be needed.

It is possible to protonate PPh_3, using highly acidic solutions (approximately pH 0), giving $[HPPh_3]^+$ which is soluble in water, removing the need for an organic solvent to be used. The ligand would be deprotonated again when the pH rose on addition of alkali, precipitating out PPh_3 again. The ligand should now be present as a very fine dispersion of the solid which will increase the reactivity. The drawback to this process is the requirement of much more Neutramag to neutralise the acidity before metal precipitation could occur. This makes this idea very inefficient. Addition of groups to the ligand that would increase the solubility in water may be possible i.e. hydroxy, sulphonate, or phosphate groups. These would also interfere with the donating properties of the ligands, however, rendering them less effective.

It was seen that as more ligand was added, the greater the increase in the rate of reaction. A set of reactions was performed to observe the limits of adding ligands, and showed that there was no increase upon using a lower ratio than approximately 80:1 (Fe^{2+}:PPh_3), **Figure 1.14**.

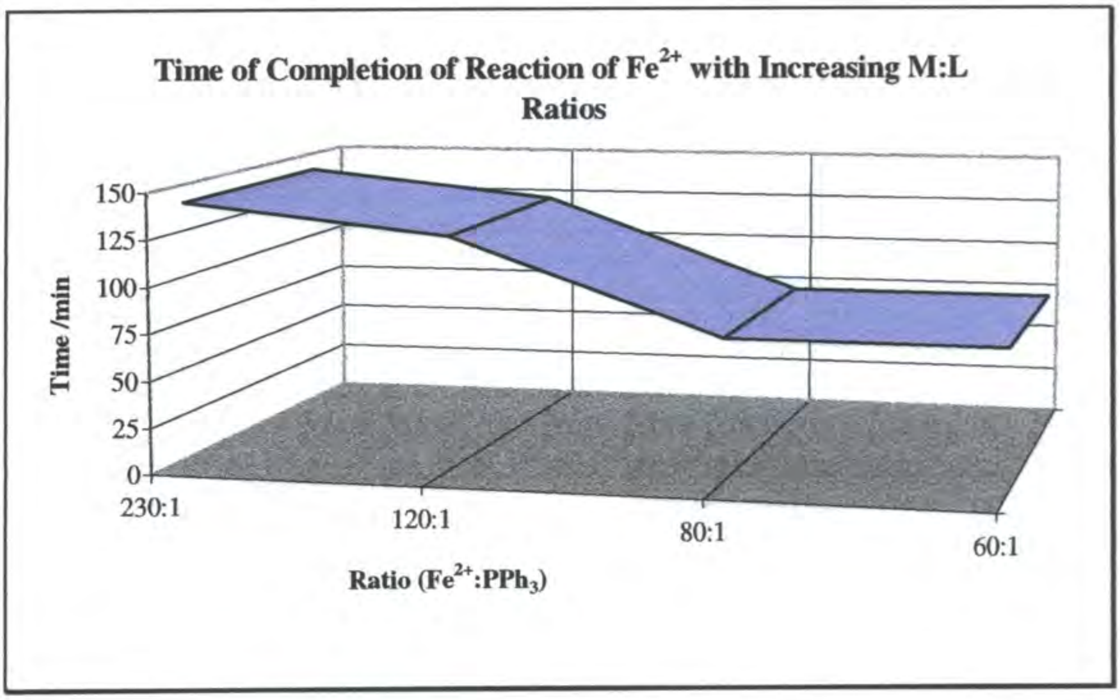
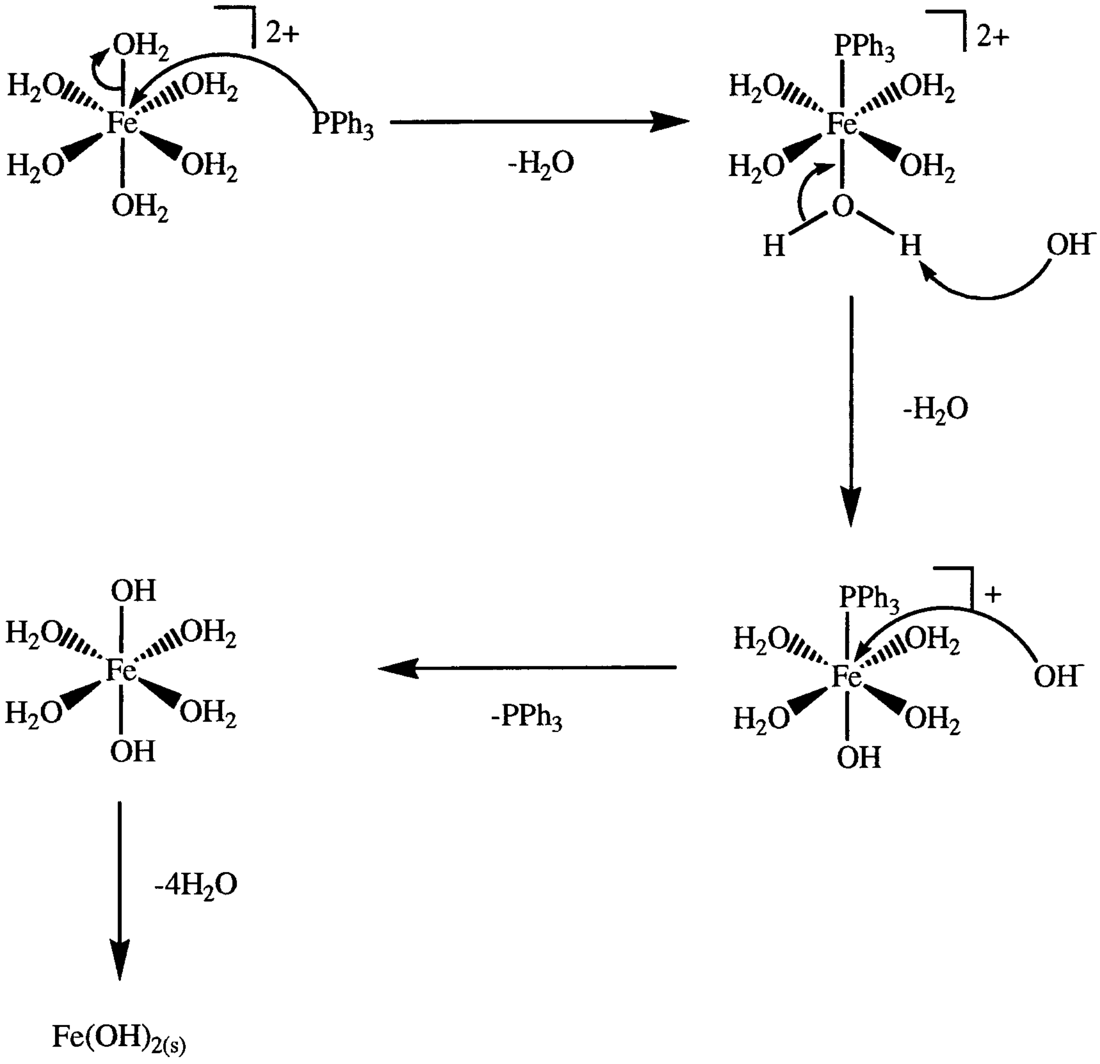


Figure 1.14

After studying the results and the way the reactions proceeded, the following mechanism was put forward as the more likely reaction pathway for the ligand interaction, **Scheme 1.2**.



Scheme 1.2 Catalytic Reaction of Fe^{2+} with PPh$_3$

The effect of the ligand is certainly catalytic in nature, much less than stoichiometric amounts being required to affect the reaction. Any ligand added must therefore be removed before final precipitation of the metal hydroxide.

The ligand species displaces one of the aquo ligands from the complex. As the new ligand is a better electron donor than water its bond with the metal will be stronger, making the aquo ligand *trans* to its bond weaker. This aquo ligand is then more susceptible to proton abstraction by the hydroxide ions in solution.

1.5 Initial Aims of the Project.

The increases in reactivity seen with the use of catalytic amounts of donor ligands were very interesting. The studies on these ligands had only been done on complex, multi-metal systems. To better qualify the observations, reactions using single metal solutions, altering the ligands used, M:L ratios and the stoichiometric amounts of Neutramag added were thought the best place to start.

It was thought that although PPh_3 had shown the most beneficial effects on the solutions, these results were obtained solely from solutions containing mainly Fe(II) and so solutions containing mostly other metals may react more favourably with other ligands. The use of N-donor ligands with harder metal centres, such as Zn(II), may give better results than the softer P-donor, PPh_3. From these reactions it was hoped that a list of combinations of metals and additives could be found so that any given solution containing mainly any given ion could be treated quickly, simply and cheaply.

It was also hoped that during the course of these studies, the reason behind the failure of Neutramag to react completely with some metal ions could be identified. This understanding could help to find a complete remedy for the reactions without the need for extra reactants.

Chapter 2

Experimental

2. Experimental

2.1 Neutramag Concentrations.

The raw Neutramag comes in the form of a slurry, but with vigorous stirring, a homogeneous suspension can be obtained and hence the amount of OH^- per unit volume can be determined and recorded as a concentration.

The raw slurry comes in concentrations of approximately 6M $Mg(OH)_2$. As most of the reactions were performed at concentrations of the order of 10^{-2}M, this slurry was taken and diluted with deionised water. These diluted slurries were vigorously stirred to give homogeneous suspensions which could be treated as having constant concentrations throughout the samples and did not settle. The concentrations of these diluted Neutramag suspensions were determined by back titration.

The procedure for these titrations is as follows. 10ml of Neutramag were taken and 10ml aliquots of volumetric HNO_3 (usually 0.996M) were added until the solid in the suspension was completely dissolved. A few drops of phenolphthalein indicator solution were added to check that the solution was acidic. If the solution was still basic, the solution turned purple; a further aliquot of HNO_3 was then added. Volumetric NaOH (usually 1.010M) was titrated into the solution until the end point was reached, the solution just turning purple. From the amount of NaOH added the amount of excess acid present could be found, and the amount of acid needed to neutralise the OH^- in the Neutramag calculated. This enables the concentration of OH^- and hence $Mg(OH)_2$ to be determined. As the pH of the titration increases, the solution turns slightly yellow as the $Mg(OH)_2$ starts to precipitate out again. This can make the end point harder to determine, although addition of extra indicator helps to identify it.

The phenolphthalein indicator solution was prepared by dissolving 2.5g (7.85×10^{-3}mol) of phenolphthalein in 500ml of 1:1 ethanol/water solution.

2.2 Excesses of Neutramag.

Throughout this work the amount of Neutramag added to the reactions is quoted in both absolute quantity and percentage excess relative to the amount of metal ions present.

The excess is calculated as follows. 1 mol of $M^{n+}_{(aq)}$ is taken to require n mol of OH^- to fully precipitate $M(OH)_{n(s)}$. This is an idealised case, which is true only if the metal ions precipitate out at pH 7. Metal ions which form hydroxides with higher K_{SP}s require higher pHs in order to precipitate completely, and those with lower K_{SP}s require lower pHs. In the experiments performed, however, the metal ions are present in initial concentrations of between $1\times10^{-3}M - 4\times10^{-2}M$, and the variations of pH between 5 and 9, the pHs at which the metals precipitate, involve changes in $[OH^-]$ of ~ $10^{-5}M$. These differences are negligible in these systems and have been ignored during the calculations.

A quote of a 10% excess of Neutramag indicates the use of n × 1.1, i.e. 110% of the amount calculated.

In most cases the initial pH is not taken into account when considering the amount of Neutramag needed to precipitate the metal ions as the solutions are from known, controlled sources. The lower pHs seen in these metal solutions are the result of deprotonation of bound waters on the metal ions, **Figure 2.1**.

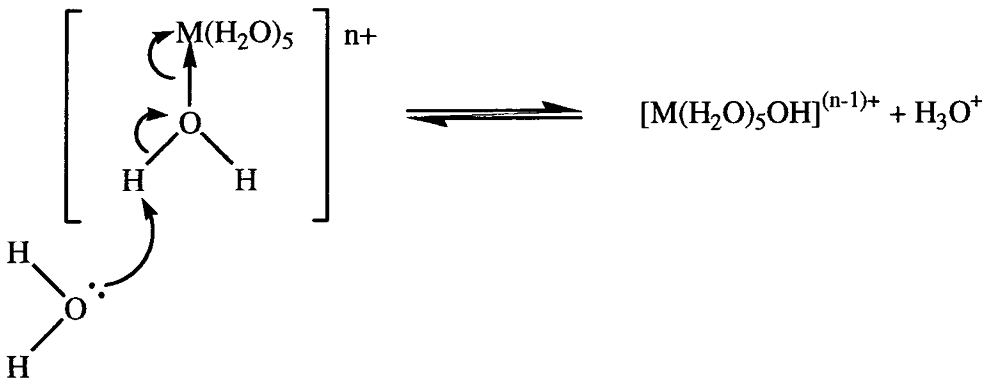


Figure 2.1 Deprotonation of Hexa-Aqua M(II) Species

For extremely hard metal centres, e.g. Al^{3+}, pHs in the region of 2 can be achieved with approximately 4×10^{-2}M $Al^{3+}_{(aq)}$. This indicates that approximately one quarter of the metals ions have had a bound water deprotonated. The hydroxonium ions formed in this way do not require neutralising as they are counter-balanced in the calculations by requiring less OH^- to precipitate the metal ions.

Where the systems contained extra, unknown quantities of acid species, either added or already present in an effluent, the initial pH was taken into account when calculating the amount of Neutramag required. This was done by measuring the pH of the initial solution and calculating the amount of H^+ present. The amount of Neutramag needed to neutralise this acidity was added on top of the excess required for metal precipitation. This led to slightly higher excesses than have been quoted in these cases as the simple metal solutions are already acidic.

In later sections of this work, excesses are calculated for reactions involving multiple metal ions. In the cases where one metal is easily precipitated, those with pK_{SP}s above 18, such as $Al^{(III)}$, $Fe^{(III)}$, $Cu^{(II)}$, only a stoichiometric amount of Neutramag has been added for this species. The quoted % excess of Neutramag used is for the more difficult to precipitate metal ion.

e.g. 1.70×10^{-2}moles of Ni^{2+} solution and 1.57×10^{-2}moles of Cu^{2+} solution require

amount of Neutramag to precipitate Ni^{2+} ions	1.70×10^{-2}moles
× 1.1 for 10% excess	
	1.87×10^{-2}moles
amount of Neutramag to precipitate Cu^{2+} ions	1.57×10^{-2}moles
	--------------------
amount of Neutramag required for a 10% excess for Ni^{2+} ions only	3.44×10^{-2}moles

2.3 Atomic Absorption Spectrophotometry.

Atomic absorption spectrophotometry was used in this project to obtain accurate values for the concentrations of metals in solutions. This technique is accurate to very low levels, i.e. less than 10 ppm.

2.3.1 Background Theory.

Atomic absorption spectrophotometry is a technique in which gaseous ground state atoms absorb radiation at a specific wavelength which produces a corresponding signal which is proportional to the concentration of ground state atoms in the optical path. [15,16]

Each element has a unique number of electrons and energy levels associated with its position in the periodic table. The electrons naturally prefer to occupy the lowest available energy levels, which give the atom the lowest energy possible. This is known as the Ground State.

If energy is introduced into the system that is equivalent to the difference between this level and a higher one, the electrons may become excited into this higher energy level. Species with electrons in higher energy levels are said to be in an Excited State, **Figure 2.2**.

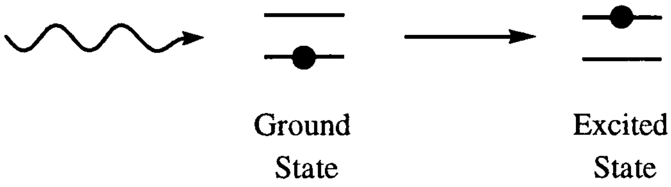


Figure 2.2 Atomic Excitation

This Excited State is not stable, however, and will readily lose energy to return to the Ground State. Although this process is almost instantaneous, the re-emitted light is released in all directions, **Figure 2.3**. Thus, from any specific direction, there is less light of that wavelength seen and this is shown as absorption when compared with other wavelengths in the spectrum.

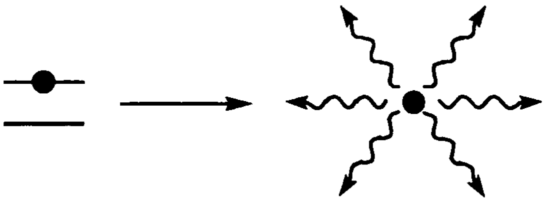


Figure 2.3 Energy Emission from Excited Atoms

Scanning through various wavelengths will show these absorbances from the species present at each wavelength that is easily absorbed. These absorption lines can then be used to identify the species.

Various wavelengths are available for each element, corresponding to the various differences between energy levels. e.g. the sodium D-lines. Scanning through a wide range of wavelengths will show all the wavelengths at which the sample will absorb which in turn gives the energy level differences. This is the absorption spectrum and can be used to identify the atom present.

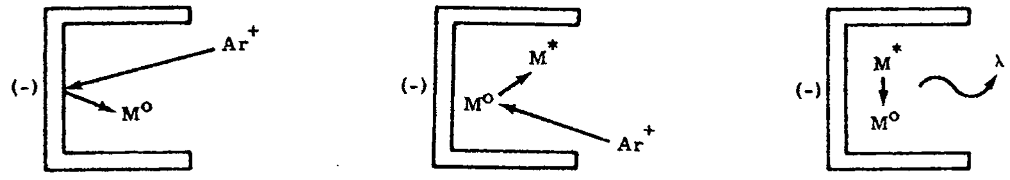
As the amount of absorption is proportional to the number of atoms absorbing and re-emitting energy of the wavelength being applied, the process can be used as a quantitative analysis as well as a qualitative one. If the wavelength being studied is absorbed strongly only by one particular element, and the other elements do not absorb near this wavelength, then all the absorption can be said to be from this element and so an accurate concentration can be obtained..

This is usually the case, but for some elements there are no clear wavelengths that absorb strongly. Titanium is one such element, and it is therefore rather tricky to obtain accurate concentrations for this metal.

Another problem is the need for light sources that approximate to the wavelength very accurately. Using even a very fine grating is not enough to keep the bandwidth of wavelengths let through sufficiently narrow. A light source emitting the relevant wavelength must be used for most elements, meaning that each element tested must have a separate lamp, although some can use the same one, e.g. calcium and magnesium.

The actual process of analysis can be broken down into several stages. Firstly the sample solution is taken through a nebulizer, and then atomised. This process is achieved by the reduced pressure at the end tube produced by the oxidant flow. The aerosol thus produced is then heated in one of a variety of ways. In these analyses an air-acetylene (or NO_2-acetylene where higher temps were required) flame was used to produce the ground state atoms needed for clear absorbance. Other atomisation process are available including electrical and graphite furnaces.

Monochromatic light is then passed through the atomised sample which absorbs the energy of the relevant wavelength to be raised to an excited state. The radiation is produced from Hollow Cathode Lamps (H.C.L.), all other wavelengths, except for the one being measured, are removed by the use of a monochromator. These lamps are constructed from hollow cylinders of the element whose spectrum is to be produced. The electrodes are sealed in a glass cylinder which is filled with a noble gas, usually neon or argon. When a potential is applied across the electrodes some of the fill gas atoms become ionized, **Figure 2.4**. These cations are then attracted to and collide with the negatively charged cathode. As a result metal atoms are dislodged from the cathode, a process known as sputtering. These free metal atoms are then excited by collisions with the fill gas and an emission spectrum is obtained from these atoms as they relax back to a lower energy state.



1. Sputtering   2. Excitation   3. Emission

Figure 2.4 Lamp Emission of Desired Wavelength

This emitted light is then broken into two separate beams, alternatively being sent down two different paths by a rotating mirror system, or "chopper", **Figure 2.5**. The first beam is transmitted directly to the monochromator, which separates the wavelength being analysed from the other wavelengths produced by the lamp and passes it through to the detection electronics. This is the reference beam. The second beam is passed through the sample before reaching the monochromator. This is the sample beam. At this point some of the light is absorbed by the atomised sample. The light reaching the monochromator is treated in exactly the same way as the reference beam. The two beams are then compared and the ratio taken. This allows fluctuations of intensity from the lamp to be ignored by the detection system, giving a much more stable baseline.

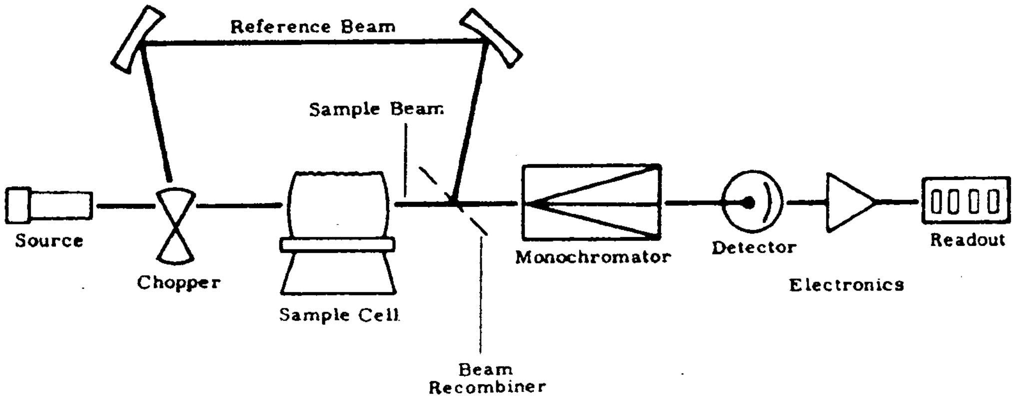


Figure 2.5 Schematic of a Double Beam Atomic Absorption Spectrophotometer

The detection system now knows how much light is being absorbed by the sample but is unable to calculate an absolute concentration without calibration. This calibration is done using two or more solutions of known concentration.

The concentration of element being analysed is proportional to the absorbance at the specific wavelength according to **Equation 2.1**.

$$A = \varepsilon c l$$

Equation 2.1

A = absorbance, ε = extinction coefficient of the test element and l is the optical path length through the sample. ε and l are fixed for an element-spectrometer combination forming a constant. However, as the concentration increases, the relationship deviates from this and is no longer linear, **Figure 2.6**. This is due to several reasons. Stray light, nonhomogeneities of temperature and space in the absorbing cell, line broadening and absorbance by nearby lines can all affect the absorbance, as can various types of inteference, **section 2.3.2**.

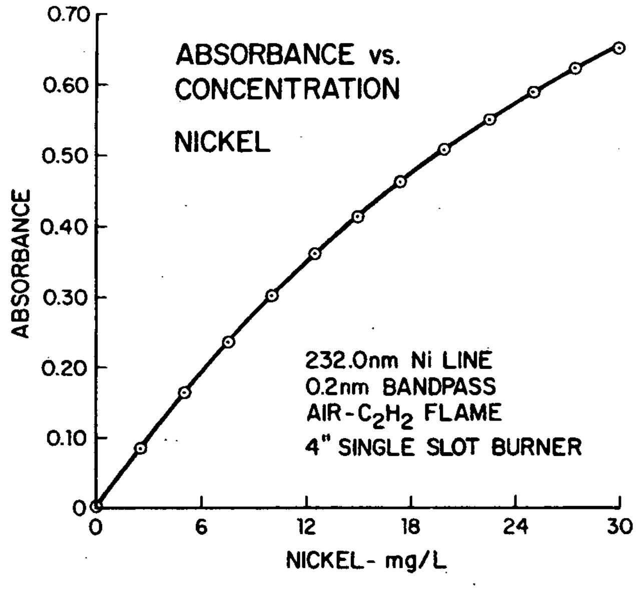


Figure 2.6 Example of Deterioration of Absorbance with Increasing Concentration

The law holds well for absorbances below 0.2. This level of absorbance corresponds to different concentrations for different elements. Calibration below these values reduces these errors. **Table 2.1** shows the concentrations of metal ions which are equivalent to 0.2 absorbance units.

Table 2.1

Metal	**Concentration approximately equivalent to 0.2 absorbance /ppm**
Copper	4.0
Iron	5.0
Nickel	7.0
Zinc	1.0
Lead	20.0
Aluminium	50.0
Chromium	4.0
Titanium	80.0
Magnesium	0.3

It is possible to use standards that are outside this range. The use of higher concentration standards allows the spectrophotometer to perform some curve correction.

2.3.2 Interferences.

There are 3 main types of interference which may occur with flame A.A.S., chemical, ionisation and spectral. [16]

Chemical interferance can be further split into 2 types. If atomisation of the sample is not complete due to occlusion into refractory compounds then less absorption will occur from entrapment by small matrix oxides. In most cases any of these compounds which are formed start to be broken up as soon as the sample enters the flame. If the compounds are require more time in the flame for complete atomisation than is available before reaching the observation height then interference will occur. Changing the observation height is often sufficient to overcome the problem.

He second type of chemical interference arises from the reaction of atoms, or radical species, which could form less volatile species. A well known example of this is the analysis of Ca in the presence of PO_4^{3-}. The interference shows up as a "knee" in plots with of increasing PO_4^{3-} concentration vs signal due to the formation of a less volatile compound, $Ca_3(PO_4)_2$. Increasing the temperature of the flame or addition of protecting species to the sample, either in the form of La^{3+} or Sr^{2+} to remove the PO_4^{3-}, or EDTA to react with the Ca^{2+} and prevent any other reactions until atomisation, will remove this problem.

Ionisation interference occurs in species with low ionisation energies, such as the alkali metals. These elements can be ionised in the atomisation flame. This partly ionised sample will give a decrease in signal due to a lower population of atoms in the GS.

Use of a cooler flame to prevent this ionisation where it is viable, however many of these species require the use of hot flames for atomisation. The equilibrium of ionisation can be altered by producing a large excess of electrons in the flame. This can be done by charge transfer or addition of a large amount of easily ionised species to both sample and reference.

Spectral interferences are due to the overlapping of emission lines from other species present in the sample which have very similar wavelengths for absorbance. They can also be caused by molecular absorbances, rotational or vibrational, of species which have not completely decomposed in the flame. These extra absorbances at the studied wavelength would give higher readings and thus concentrations than were actually obtained from the sample.

2.3.3 Atomic Absorption Spectrophotometry Configurations.

The work here was done on a Perkin Elmer 5000 Atomic Absorption Spectrophotometer, using Perkin Elmer Intensitron lamps. The wavelengths of observation, the slit widths, the currents, energy readings and concentrations of standards used are listed in **Table 2.2**.

Table 2.2

Metal	Wavelength used /nm	Slit width used	Current /mA	Approximate energy reading	Concentration of standard solution /ppm
Copper	324.8	0.7	15	65	2.00
Iron	248.3	0.2	30	55	5.00
Nickel	232.0	0.2	25	55	5.00
Zinc	213.9	0.7	15	60	1.00
Lead	283.3	0.7	10	65	20.0
Aluminium	309.3	0.7	10	55	40.0
Chromium	357.9	0.7	25	70	5.00
Titanium	364.3	0.2	10	50	12.0
Magnesium	285.2	0.7	15	60	0.5

2.4 Accuracy of Results

In each of the sets of reactions performed, several factors must be taken into consideration with regards to the absolute accuracy of the readings. As the AA will only give accurate readings in the region of 1-10ppm for various elements and the final solutions obtained after reaction and filtration were often in the 100s off ppm, some dilution was required. Each filtrate was kept in sealed containers until the entire set of reactions were ready for analysis. The samples were then diluted and analysed in the same session of the AA. This helped to reduce any errors which could arise from performing the analysis at separate times.

Unless otherwise mentioned, samples of the solution were taken using an adjustable 1ml pipette, which measured with an accuracy of ± 0.005ml, of volumes related to the maximum usable concentration and diluted to 100ml using deionised water. E.g. Ni max. concentration = 5ppm ∴ use 0.50ml in 100ml, giving a reading of 5ppm equivalent to a concentration of 1000ppm, the usual starting concentration. The fraction of this 5ppm reading attained was the same fraction of the starting solution and hence the final concentration could be calculated. When the levels achieved were low enough, lower dilutions were used and in some cases the raw, undiluted filtrate was analysed.

The samples were tested several times on the AA spectrometer and an average of the results taken. The values for these readings varied by no more than ±0.02ppm. Any greater variations than that meant that the sample was rediluted and analysed again. These variations in readings when combined with the dilution give accuracies of ±4ppm. This is negligible for most reactions where the final concentrations are in the high 100s of ppm.

As the goal of the project was the improvement of the reactions, the relative concentrations were of more importance than the absolute values and so, as long as the conditions for a set of reactions remained constant, the results could be clearly seen. Most sets of results showed clear trends and were well outside the errors discussed here.

2.5 pH Equipment.

Throughout this work pHs were measured using a Jenway 3020 pH meter with BDS Gelplas electrodes. The electrode was calibrated before each reaction using buffer solutions of pH 4 and pH 9.2. Whilst not in use the electrode was kept in a acidic solution to remove any oxides or hydroxides which had adhered to it in previous reactions.

2.6 Preparation of Solutions.

The metal ion solutions which were used in this project were made from the dissolution of the relevant salts in deionised water. Each of the salts were obtained from Aldrich Chemicals as A.C.S. reagents. The amount of salt required to give 10g of metal ion was taken and dissolved to a volume of 1000ml, giving an approximate concentration of 10,000ppm. **Table 2.3** shows the masses used and their purities.

Table 2.3

Metal Ion	Salt Used	Mass Used /g	Purity /%
Al^{3+}	$Al(NO_3)_3.9H_2O$	139.04	98+
	$Al_2(SO_4)_3.18H_2O$	123.50	98+
Cu^{2+}	$CuSO_4.5H_2O$	39.29	98+
Fe^{2+}	$FeSO_4.5H_2O$	49.78	99+
Fe^{3+}	$Fe(NO_3)_3.9H_2O$	72.34	98+
Ni^{2+}	$NiSO_4.6H_2O$	44.79	99+
Pb^{2+}	$Pb(NO_3)_2$	15.99	99+
Zn^{2+}	$Zn(NO_3)_2.6H_2O$	45.50	98+

The donor ligands used in some of the reactions in this project were often insoluble in aqueous solution. They were therefore prepared by dissolving (or diluting) the relative amounts in acetone.

The triphenylphosphine (PPh_3) solutions were prepared at concentrations of 1.0×10^{-2}M, 1.6×10^{-2}M and 1.7×10^{-2}M. 0.26g (1.0×10^{-3}mol), 0.41g (1.6×10^{-3}mol) and 0.45g (1.7×10^{-3}mol) of PPh_3 were taken respectively and dissolved to volumes of 100ml with acetone.

The N,N,N',N'-tetramethylethylenediamine (TMEDA) solutions were prepared at concentrations of 1.6×10^{-2}M and 1.7×10^{-2}M. 0.24ml (1.6×10^{-3}mol) and 0.26ml (1.7×10^{-3}mol) of TMEDA were taken respectively, ($\rho_{TMEDA} = 0.77g.dm^{-3}$), and diluted to volumes of 100ml with acetone.

The 2,2'-bipyridine (bipy) solutions were prepared at concentrations of 1.6×10^{-2}M and 1.7×10^{-2}M. 0.25g (1.6×10^{-3}mol) and 0.27g (1.7×10^{-3}mol) of bipy were taken respectively and dissolved to a volume of 100ml with acetone.

The 1,2-bis(diphenylphosphino)ethane (dppe) solution was prepared at a concentration of 1.0×10^{-2}M. This was done by weighing out a 0.40g sample of solid dppe and dissolving it in 100ml of acetone.

Chapter 3

Studies on Single Metal Systems

3. Single Metal Reactions.

The reactions of Neutramag with simple single metal systems were initially examined. The previous project had concentrated on more complex, multiple metal systems; whilst these were more realistic, real industrial effluents often containing more than one metal ion, it was more difficult to interpret their results. This part of the project would look at the different metal ions individually and compare the results as variables, such as excess of Neutramag, ligand addition etc., were changed.

3.1 Copper.

The first metal to be studied was copper. As one of the industrial effluents currently being studied by Redland contained mainly copper ions, but only at a concentration of approximately 50ppm, most of the copper reactions were performed at the 100ppm level, so as to give a better comparison.

The results for this section are discussed in **section 3.8.1**.

3.1.1 Preparation of Standard Cu^{2+} Solution.

A standard concentrated solution of 10,000ppm copper was prepared by dissolving 39.29g of $CuSO_4.5H_2O$ in 1000ml of demineralised water. This solution is equivalent to 1.57×10^{-1}M Cu^{2+}. 1ml of this solution was taken and diluted into 100ml. 1ml of this diluted solution was taken and diluted again into 100ml to give a solution of approximately 1ppm. This solution was then analysed using atomic absorption to obtain an accurate concentration of 1.00ppm. The stock solution was therefore 10,000ppm Cu^{2+} (1.57×10^{-1}M).

3.1.2 Reactions with Large Excesses of Neutramag.

3.1.2.1 Reaction Using No Ligand.

10ml of 10,000ppm Cu^{2+} solution (1.57×10^{-3}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Cu^{2+} concentration of 100ppm, (1.57×10^{-3}M). The pH of this solution was recorded. 7.5ml of Neutramag slurry (2.75×10^{-3}mol) were added to the solution. giving a 75% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of copper remaining in the filtrate determined by atomic absorption. The results are shown in **Table 3.1**.

Table 3.1

% excess of Neutramag used	Ligand added	Initial pH	Final pH	Time /min	Final copper concentration /ppm
75	NONE	4.46	8.40	34	0.32

3.1.2.2 Reaction Using PPh_3.

10ml of 10,000ppm Cu^{2+} solution (1.57×10^{-3}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Cu^{2+} concentration of 100ppm, (1.57×10^{-3}M). The pH of this solution was recorded. 1ml of PPh_3 solution (1.57×10^{-5}mol) was added and allowed to mix with the solution before the pH was measured again. This gave a Cu^{2+}:PPh_3 ratio of 100:1. 7.5ml of Neutramag slurry (2.75×10^{-3}mol) were added to the solution. giving a 75% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of copper remaining in the filtrate determined by atomic absorption. The results are shown in

Table 3.2.

Table 3.2

% excess of Neutramag used	Ligand added	Initial pH	Final pH	Time /min	Final copper concentration /ppm
75	PPh_3	4.39	8.71	32	0.11

3.1.3 Reactions with Smaller Excesses of Neutramag.

3.1.3.1 Reaction Using No Ligand.

10ml of 10,000ppm Cu^{2+} solution (1.57×10^{-3}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Cu^{2+} concentration of 100ppm, (1.57×10^{-3}M). The pH of this solution was recorded. 5.0ml of Neutramag slurry (1.84×10^{-3}mol) were added to the solution. giving a 17% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of copper remaining in the filtrate determined by atomic absorption. The results are shown in **Table 3.3**.

Table 3.3

% excess of Neutramag used	Ligand added	Initial pH	Final pH	Time /min	Final copper concentration /ppm
17	NONE	4.58	7.91	60	0.00

3.1.3.2 Reactions Using PPh_3.

10ml of 10,000ppm Cu^{2+} solution (1.57×10^{-3}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Cu^{2+} concentration of 100ppm, (1.57×10^{-3}M). The pH of this solution was recorded. 1.0ml of PPh_3 solution (1.57×10^{-5}mol) was added and allowed to mix with the solution before the pH was measured again. These gave a Cu^{2+}:PPh_3 ratio of 100:1. 5.0ml of Neutramag slurry (1.84×10^{-3}mol) were added to the solution, giving a 17% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of copper remaining in the filtrate determined by atomic absorption.

This reaction was repeated using decreasing amounts of PPh_3. The Cu^{2+}:PPh_3 ratios used were 100:1 (1.0ml, 1.57×10^{-5}mol), 500:1(0.2ml, 3.14×10^{-6}mol) and 1000:1 (0.1ml, 1.57×10^{-6}mol).

The results are shown in **Table 3.4**.

Table 3.4

Volume of PPh_3 used /ml	**Cu^{2+}:PPh_3 ratio**	**Initial pH**	**Final pH**	**Time /min**	**Final copper concentration /ppm**
1.0	100:1	4.42	7.93	180	1.80
0.2	500:1	4.22	7.67	60	0.36
0.1	1000:1	4.22	7.77	60	0.34

3.1.3.3 Reactions Using TMEDA.

10ml of 10,000ppm Cu^{2+} solution (1.57×10^{-3}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Cu^{2+} concentration of 100ppm, (1.57×10^{-3}M). The pH of this solution was recorded. 10.0ml of TMEDA solution (1.57×10^{-4}mol) were added and allowed to mix with the solution before the pH was measured again. This gave a Cu^{2+}:TMEDA ratio of 10:1. 5.0ml of Neutramag slurry (1.84×10^{-3}mol) were added to the solution, giving a 17% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of copper remaining in the filtrate determined by atomic absorption.

This reaction was repeated using decreasing amounts of TMEDA. The Cu^{2+}:TMEDA ratios used were 100:1 (1.0ml, 1.57×10^{-5}mol) and 1000:1 (0.1ml, 1.57×10^{-6}mol).

The results are shown in **Table 3.5**.

Table 3.5

Volume of TMEDA used /ml	Cu^{2+}:TMEDA ratio	Initial pH	Final pH	Time /min	Final copper concentration /ppm
10	10:1	5.28	7.89	100	11.0
1	100:1	4.75	7.64	100	2.00
0.1	1000:1	4.25	7.82	90	0.51

3.1.3.4 Reactions Using Other Chelating Ligands.

10ml of 10,000ppm Cu^{2+} solution (1.57×10^{-3}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Cu^{2+} concentration of 100ppm, (1.57×10^{-3}M). The pH of this solution was recorded. 1ml of bipy solution (1.57×10^{-5}mol) was added to separate reactions and allowed to mix with the solution before the pH was measured again. This gave a Cu^{2+}:bipy ratio of 100:1. 5.0ml of Neutramag slurry (1.84×10^{-3}mol) were added to the solution, giving a 17% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of copper remaining in the filtrate determined by atomic absorption.

The reaction was repeated using 1.0ml of DPPE solution (1.75×10^{-5}mol), giving a Cu^{2+}:DPPE ratio of 100:1.

The results are shown in **Table 3.6**.

Table 3.6

Ligand added	**Cu^{2+}:ligand ratio**	**Initial pH**	**Final pH**	**Time /min**	**Final copper concentration /ppm**
Bipy	100:1	4.36	7.63	60	0.15
DPPE	100:1	4.30	7.52	100	10.2

3.1.4 Reaction At Higher Concentration.

100ml of 10,000ppm Cu^{2+} solution (1.57×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Cu^{2+} concentration of 1000ppm, (1.57×10^{-2}M). The pH of this solution was recorded. 5.0ml of Neutramag slurry (1.84×10^{-2}mol) added to the solution. giving a 17% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of copper remaining in the filtrate determined by atomic absorption.

The results are shown in **Table 3.7**.

Table 3.7

% excess of Neutramag used	Ligand added	Initial pH	Final pH	Time /min	Final copper concentration /ppm
17	NONE	3.22	9.58	16	0.22

3.2 Industrial Sample 1.

This set of reactions was performed on an actual effluent sent to Britmag for analysis and treatment. Discussion of the results can be found in **3.8.2**.

3.2.1 Determination of Copper Concentration.

The neat effluent solution was analysed using atomic absorption, showing that it contained 49ppm copper, (7.71×10^{-4}M).

3.2.2 Reactions with Diluted Samples.

3.2.2.1 Reactions Using High Excesses of Neutramag.

3.2.2.1.1 Reaction with No Ligand.

100ml of effluent sample (7.71×10^{-5}mol Cu^{2+}) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Cu^{2+} concentration of 4.9ppm, (7.71×10^{-5}M). The pH of this solution was recorded and used to calculate the concentration of acid present as described in **section 2.2**. 5.0ml of Neutramag slurry (1.84×10^{-3}mol) were added to the solution. giving a 1570% excess for complete stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of copper remaining in the filtrate determined by atomic absorption.

The results are shown in **Table 3.8**.

Table 3.8

Volume of Neutramag used /ml	% excess of Neutramag used	Initial pH	Final pH	Time /min	Final copper concentration /ppm	% copper removed
5.0	1700	2.98	7.18	95	1.86	62

3.2.2.1.2 Reaction Using PPh_3.

100ml of effluent sample (7.71×10^{-5}mol Cu^{2+}) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Cu^{2+} concentration of 4.9ppm, (7.71×10^{-5}M). The pH of this solution was recorded and used to calculate the concentration of acid as described in **section 2.2**. 5.0ml of PPh_3 solution (7.85×10^{-7}mol) were added to the solution and allowed to mix before the pH was recorded again. 5.0ml of Neutramag slurry (1.84×10^{-3}mol) were added to the solution. giving a 1570% excess over that needed for complete stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of copper remaining in the filtrate determined by atomic absorption.

The reaction was repeated using 10.0ml of PPh_3 solution (1.57×10^{-6}mol) and 10.0ml of Neutramag slurry (3.68×10^{-3}mol), giving a Cu^{2+}:PPh_3 ratio of 50:1 and a 4055% excess over that needed for full stoichiometric reaction.

The results are shown **Table 3.9**.

Table 3.9

Volume of Neutramag used /ml	**% excess of Neutramag used**	**Initial pH**	**Final pH**	**Time /min**	**Final copper concentration /ppm**	**% copper removed**
5.0	1570	2.96	7.28	100	0.97	80
10.0	4055	3.03	7.98	135	0.30	94

3.2.2.2 Reactions Using Smaller Excesses of Neutramag.

3.2.2.2.1 Reactions With No Ligand.

100ml of effluent sample (7.71×10^{-5}mol Cu^{2+}) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Cu^{2+} concentration of 4.9ppm (7.71×10^{-5}M). The pH of this solution was recorded and used to calculate the concentration of acid as described in **section 2.2**. 2.0ml of Neutramag slurry (0.37M; 7.34×10^{-4}mol) were added to the solution, giving a 300% excess over that needed for complete stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of copper remaining in the filtrate determined by atomic absorption.

This reaction was repeated using increasing amounts of Neutramag slurry. The aliquots used were 1.5ml of (0.66M; 1.02×10^{-3}mol), 3.0ml (0.37M; 1.10×10^{-3}mol) and 4.0ml (0.37M; 1.47×10^{-4}mol) which gave 439%, 725% and 950% excesses, respectively, over that needed for complete stoichiometric reaction

The results are shown in **Table 3.10**.

Table 3.10

Volume of Neutramag used /ml	% excess of Neutramag used	Initial pH	Final pH	Time /min	Final copper concentration /ppm	% copper removed
2.0	300	3.07	6.80	100	3.10	37
1.5	439	2.92	7.01	100	2.30	53
3.0	723	3.03	6.97	100	2.00	59
4.0	950	2.88	7.05	100	1.29	74

3.2.2.2.2 Reactions With PPh_3.

100ml of effluent sample (7.71×10^{-5}mol Cu^{2+}) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Cu^{2+} concentration of 4.9ppm (7.71×10^{-5}M). The pH of this solution was recorded and used to calculate the concentration of acid as described in **section 2.2.** 5.0ml of PPh_3 solution (7.85×10^{-7}mol) were added and allowed to mix before the pH was measured again. 2.0ml of Neutramag slurry (0.37M; 7.34×10^{-4}mol) were added to the solution, giving a 124% excess over that needed for complete stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of copper remaining in the filtrate determined by atomic absorption.

This reaction was repeated using increasing excesses of Neutramag. The amounts of Neutramag used were 1.2ml (0.66M; 8.18×10^{-4}mol) and 3.0ml (0.37M; 1.10×10^{-3}mol) which gave 250% and 530% excesses, respectively, over that needed for complete stoichiometric reaction.

The results are shown in **Table 3.11**.

Table 3.11

Volume of Neutramag used /ml	% excess of Neutramag used	Initial pH	Final pH	Time /min	Final copper concentration /ppm	% copper removed
2.0	124	2.95	6.81	100	2.70	45
1.24	250	2.96	6.86	100	2.30	45
3.0	530	2.91	6.92	110	2.10	57

3.2.3 Reactions Using Undiluted Effluent Samples.

3.2.3.1 Reactions at 500% Excess.

500ml of effluent sample (3.86×10^{-4}mol Cu^{2+}) were taken. This gave an initial Cu^{2+} concentration of 49ppm, (7.71×10^{-4}M). The pH of this solution was recorded and used to calculate the concentration of acid present as described in **section 2.2**. 8.37ml of Neutramag slurry (5.52×10^{-3}mol) were added to the solution. giving a 477% excess for complete stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of copper remaining in the filtrate determined by atomic absorption.

The reactions were repeated using PPh_3 and TMEDA in 1000:1 Cu^{2+}:L ratios. 2.5ml of PPh_3 solution (3.93×10^{-7}mol) and 2.5ml of TMEDA solution (3.93×10^{-7}mol) were added.

The results are shown in **Table 3.12**.

Table 3.12

Volume of Neutramag used /ml	% excess of Neutramag used	Ligand added	Initial pH	Final pH	Time /min	Final copper concentration /ppm	% copper removed
8.37	477	NONE	1.88	7.05	100	5.5	89
8.40	502	PPh_3	1.89	7.04	100	6.2	87
8.90	507	TMEDA	1.85	7.09	100	5.5	89

3.2.3.2 Reactions with Lower Excesses.

500ml of effluent sample (3.86×10^{-4}mol Cu^{2+}) were taken. This gave an initial Cu^{2+} concentration of 49ppm, (7.71×10^{-4}M). The pH of this solution was recorded and used to calculate the concentration of acid present as described in **section 2.2**. 7.5ml of Neutramag slurry (4.95×10^{-3}mol) were added to the solution. giving a 107% excess for complete stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of copper remaining in the filtrate determined by atomic absorption.

The reaction was repeated using 9.0ml of Neutramag,. giving a 233% excess for complete stoichiometric reaction.

The results are shown in **Table 3.13**.

Table 3.13

Volume of Neutramag used /ml	% excess of Neutramag used	Initial pH	Final pH	Time /min	Final copper concentration /ppm	% copper removed
7.5	107	1.78	6.82	100	10.3	79
9.0	233	1.73	7.53	180	4.30	94

3.2.3.3 Treatment with Hydrogen Peroxide.

3.2.3.3.1 Preparation of Solution.

3.93g of $CuSO_4.5H_2O$, 25ml of 0.987M HNO_3 and 30ml of 0.52M NH_3 were taken and diluted to a volume of 1000ml with deionised water. This solution was equivalent to approximately 1.57×10^{-2}M Cu^{2+}. 4.0ml of this solution was taken and diluted to a volume of 1000ml. This solution was then analysed using atomic absorption to obtain an accurate concentration of 3.85ppm. The stock solution was therefore 963ppm Cu^{2+} (1.51×10^{-2}M). This solution was called ISL 2.

3.2.3.3.2 Reactions of Artificial Solution.

100ml of ISL 2 solution were taken and diluted to a volume of 1000ml with deionised water. This gave an initial concentration of 1.51×10^{-3}M Cu^{2+}, 1.51×10^{-3}M NH_3 and 2.47×10^{-3}M HNO_3. This was equivalent to a $Cu^{2+}:NH_3$ ratio of 1:1. The pH of this solution was recorded. 1.1ml of Neutramag slurry (2.89×10^{-3}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction. The reaction was stopped by filtration after 60 minutes and the concentration of copper remaining in the filtrate determined by atomic absorption.

The reaction was repeated with extra NH_3 being added. 3.0ml (1.53×10^{-3}mol) and 9.0ml (4.59×10^{-3}mol) were added to the solution giving $Cu^{2+}:NH_3$ ratios of 1:2 and 1:4 respectively.

The initial reaction was repeated again with the addition of 8.0ml of 3% H_2O_2 solution (6.04×10^{-3}mol). This gave an $NH_3:H_2O_2$ ratio of 4:1.

The results are shown in **Table 3.14**.

Table 3.14

Volume of NH_3 added /ml	Volume of H_2O_2 added /ml	Initial pH	Final pH	Time /min	Final copper concentration /ppm
0.0	0.0	2.18	8.45	60	0.22
3.0	0.0	2.16	8.55	60	0.12
9.0	0.0	2.35	8.73	60	0.08
0.0	8.0	2.22	9.36	60	0.05

3.3 Iron.

Cooling and washing waters from steel works often contain large amounts of iron(II) and must be treated.

The discussion for the results in this section is found in **section 3.8.3**.

3.3.1 Preparation of Standard Fe^{2+} Solution.

A standard concentrated solution of 10,000ppm Fe^{2+} was prepared by dissolving 49.78g of $FeSO_4.7H_2O$ in 500ml of demineralised water. A few drops of concentrated sulphuric acid were added to lower the pH. As iron(II) is far less susceptible to oxidation at very low pH, the acid should prevent the stock solution from going off. The solution was then made up to 1000ml. This solution was equivalent to 1.79×10^{-1}M Fe^{2+}. 1ml of this stock solution was taken and diluted into 100ml. 1ml of this diluted solution was taken and diluted again into 100ml to give a solution of approximately 1ppm. This solution was then analysed using atomic absorption to obtain an accurate concentration of 1.00ppm. The stock solution was therefore 10,000ppm.

3.3.2 Aeration Reactions.

100ml of 10,000ppm Fe^{2+} solution (1.79×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. The pH of this solution was then recorded and used to calculate the concentration of acid as described in **section 2.2**. 40.0ml of Neutramag slurry (2.64×10^{-2} mol) were added to the solution, giving an 18% excess over that needed for complete stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of iron remaining in the filtrate determined by atomic absorption.

This reaction was repeated using differing amounts of aeration. Aeration was applied by passing compressed air through a piece of perforated tubing immersed in the solution. The aeration was applied after the addition of the Neutramag for one reaction and for 5 minutes prior to addition of Neutramag in another. 40.0ml of Neutramag were added to each reaction.

The results are shown in **Table 3.15**.

Table 3.15

% excess of Neutramag added	Bubbling used	Initial pH	Final pH	Time /min	Final iron concentration /ppm	% iron removed	Colour of precipitate
18	None	1.97	7.28	20	590	41	Green
14	During reaction ONLY	1.92	6.07	10	420	58	Brown
8	Before and during reaction	1.85	6.16	5	550	45	Brown

100ml of 10,000ppm Fe^{2+} solution (1.79×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. The pH of this solution was then recorded and used to calculate the concentration of acid as described in **section 2.2**. 40.0ml of Neutramag slurry (2.64×10^{-2}mol) were added to the solution giving a 9% excess over that needed for complete stoichiometric reaction. The reaction mixture was left to react for 90 minutes, irrespective of the pH. The solution was then filtered and the concentration of iron remaining in the filtrate determined by atomic absorption.

The results are shown in **Table 3.16**.

Table 3.16

% excess of Neutramag added	Bubbling used	Initial pH	Final pH	Time /min	Final iron concentration /ppm	% iron removed	Colour of precipitate
9	During reaction ONLY	1.86	5.03	90	80	92	Brown

3.3.3 Reactions Using PPh_3.

100ml of 10,000ppm Fe^{2+} solution (1.79×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. The pH of this solution was then recorded and used to calculate the concentration of acid as described in **section 2.2**. 16.5ml of Neutramag slurry (2.74×10^{-2}mol) were added to the solution, giving a 26% excess over that needed for complete stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of iron remaining in the filtrate determined by atomic absorption.

This reaction was repeated with the addition of 11.4ml of PPh_3 solution (1.79×10^{-4}mol), giving a Fe^{2+}:PPh_3 ratio of 100:1.

The results are shown in **Table 3.17**.

Table 3.17

% excess of Neutramag added	Ligand added	Initial pH	Final pH	Time /min	Final iron concentration /ppm	% iron removed
26	NONE	2.01	7.39	18	615	39
27	PPh_3	2.02	7.30	14	510	49

3.3.4 Reactions Using Various Ligands.

100ml of 10,000ppm Fe^{2+} solution (1.79×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. The pH of this solution was then recorded and used to calculate the concentration of acid as described in **section 2.2**. 20.0ml of Neutramag slurry (3.32×10^{-2}mol) were added to the solution, giving a 26% excess over that needed for complete stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of iron remaining in the filtrate determined by atomic absorption.

This reaction was repeated but left to react for a longer period of time before filtration.

This reaction was also repeated with the addition of aliquots of various ligand solutions. 11.4ml of PPh_3 and TMEDA solutions (1.79×10^{-4}mol) and 17.9ml of DPPE solutions (1.79×10^{-4}mol) were added when necessary, giving Fe^{2+}:L ratios of 100:1

The results are shown in **Table 3.18**.

Table 3.18

% excess of Neutramag added	Ligand added	Initial pH	Final pH	Time /min	Final iron concentration /ppm	% iron removed
58	NONE	2.00	7.41	10	295	71
60	NONE	2.01	7.16	110	235	76.5
61	PPh_3	2.05	9.24	98	< 3	> 99.7
58	TMEDA	2.00	9.31	110	50	94.8
59	DPPE	2.01	9.11	110	4.1	99.6

3.4 Nickel.

The discussion for this section is found in **section 3.8.4**.

3.4.1 Preparation of Standard Ni^{2+} Solutions.

A standard concentrated solution of approximately 10,000ppm Ni^{2+} was prepared by dissolving 49.79g of $NiSO_4.6H_2O$ in 1000ml of deionised water. This solution is equivalent to 1.70×10^{-1}M Ni^{2+}. 1ml of this stock solution was taken and diluted into 100ml. 1ml of this diluted solution was taken and diluted again into 100ml to give a solution of approximately 1ppm. This solution was then analysed using atomic absorption to obtain an accurate concentration of between 1.00 and 1.06ppm. The stock solutions were therefore between 10,000ppm and 10,600ppm.

3.4.2 Reactions with No Ligands.

3.4.2.1 Reactions at 100ppm.

10ml of 10,000ppm Ni^{2+} solution (1.70×10^{-3}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 100ppm (1.70×10^{-3}M). The pH of this solution was recorded. 1.5ml of Neutramag slurry (2.50×10^{-3}mol) were added to the solution, giving a 47% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of nickel remaining in the filtrate determined by atomic absorption.

The reaction was repeated using the same amounts of reactants but was left to react for 60 minutes before filtration and analysis.
The results are shown in **Table 3.19**.

Table 3.19

% excess Neutramag used	Initial pH	Final pH	Time /min	Final nickel concentration /ppm	% nickel removed
47	6.14	8.57	30	93	7
47	6.20	8.54	60	92	8

3.4.2.2 Reactions at 1000ppm.

100ml of 10,000ppm Ni^{2+} solution (1.70×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 100ppm (1.70×10^{-2}M). The pH of this solution was recorded. 15.0ml of Neutramag slurry (1.67M; 2.50×10^{-2}mol) were added to the solution, giving a 47% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of nickel remaining in the filtrate determined by atomic absorption.

The reaction was repeated using 8.9ml (2.11M) and 100ml (0.19M) of Neutramag slurry, respectively, (1.87×10^{-2}mol) which gave 10% excesses over that needed for full stoichiometric reaction. The reactions were stopped after 30 and 210 minutes by filtration and the concentration of nickel remaining in the filtrates determined by atomic absorption.

The results are shown in **Table 3.20**.

Table 3.20

% excess Neutramag added	Initial pH	pH	Time /min	Final nickel concentration /ppm	% nickel removed
47	6.19	8.24	30	910	9
10	5.33	7.94	30	930	7
10	6.00	8.23	210	910	9

3.4.3 Reactions with Ligands.

3.4.3.1 Reactions with PPh_3.

3.4.3.1.1 Reactions at 10% Excess of Neutramag.

100ml of 10,000ppm Ni^{2+} solution (1.70×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1000ppm (1.70×10^{-2}M). The pH of this solution was recorded. 8.9ml of Neutramag slurry (1.87×10^{-2}mol) were added to the solution, giving a 10% excess over that needed for full stoichiometric reaction. A sample of approximately 80ml of the reaction mixture was taken after 30 minutes and filtered The reaction was stopped by filtration after 60 minutes and the concentration of nickel remaining in the filtrate determined by atomic absorption.

The reaction was repeated with the addition of 3.5ml of PPh_3 solution (3.5×10^{-5}mol), giving a Ni^{2+}:PPh_3 ratio of 500:1.

The results are shown in **Table 3.21**.

Table 3.21

Ligand added	**Initial pH**	**Time /min**	**pH**	**Concentration of nickel /ppm**	**% nickel removed**
None	5.33	30	7.94	930	7
		60	7.92	940	6
PPh_3	5.90	30	8.06	950	5
		60	8.04	940	6

3.4.3.1.2 Reactions at 60% Excess of Neutramag.

100ml of 10,000ppm Ni^{2+} solution (1.70×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1000ppm (1.70×10^{-2}M). The pH of this solution was recorded. 10.0ml of PPh_3 solution (1.70×10^{-4}mol) was added to the solution giving a Ni^{2+}:PPh_3 ratio of 100:1. 75.0ml of Neutramag slurry (2.78×10^{-2}mol) were added to the solution, giving a 60% excess over that needed for full stoichiometric reaction. The reaction was stopped by filtration after 130 minutes and the concentration of nickel remaining in the filtrate determined by atomic absorption.

The reaction was repeated, letting it react for 180 minutes before filtration. These reactions were then repeated using Ni^{2+}:PPh_3 ratios of 10,000:1.

A further reaction was performed with 2.0ml of PPh_3 solution (3.5×10^{-5}mol), giving a Ni^{2+}:PPh_3 ratio of 500:1, which was left to react overnight.

The results are shown in **Table 3.22**.

Table 3.22

Ni^{2+}:PPh_3 ratio	**Initial pH**	**Final pH**	**Time /min**	**Final nickel concentration /ppm**	**% nickel removed**
100:1	6.16	8.01	130	700	30
100:1	5.78	7.95	180	710	29
10000:1	5.02	7.99	130	870	13
10000:1	5.35	8.00	180	760	24
500:1	5.40	8.00	21 hours	710	29

3.4.3.2 Reactions with TMEDA.

100ml of 10,225ppm Ni^{2+} solution (1.74×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1023ppm (1.74×10^{-2}M). The pH of this solution was recorded. 17.4ml of TMEDA solution (1.74×10^{-4}mol) were added to the solution, giving a Ni^{2+}:TMEDA ratio of 100:1. 7.5ml of Neutramag slurry (1.91×10^{-2}mol) were added to the solution, giving a 10% excess over that needed for full stoichiometric reaction. A sample of approximately 80ml of the reaction mixture was taken after 30 minutes and filtered. The reaction was stopped by filtration after 60 minutes and the concentration of nickel remaining in the filtrate determined by atomic absorption.

The reaction was repeated with decreasing amounts of TMEDA solution being added. 8.7ml (8.7×10^{-5}mol) and 3.5ml (3.5×10^{-5}mol) were added to separate reactions, giving Ni^{2+}:TMEDA ratios of 200:1 and 500:1 respectively.

The results are shown in **Table 3.23**.

Table 3.23

Ni^{2+}:TMEDA ratio	**Initial pH**	**Time /min**	**pH**	**Nickel concentration /ppm**	**% nickel removed**
100:1	4.08	30	8.35	955	7
		60	8.35	945	8
200:1	4.07	30	8.40	940	8
		60	8.40	925	10
500:1	4.04	30	8.46	918	10
		60	8.46	890	13

3.4.3.3 Reactions with Bipy.

100ml of 10,225ppm Ni^{2+} solution (1.74×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1023ppm (1.74×10^{-2}M). The pH of this solution was recorded. 17.4ml of bipy solution (1.74×10^{-4}mol) were added to the solution, giving a Ni^{2+}:bipy ratio of 100:1. 7.5ml of Neutramag slurry (1.91×10^{-2}mol) were added to the solution, giving a 10% excess over that needed for full stoichiometric reaction. A sample of approximately 80ml of the reaction mixture was taken after 30 minutes and filtered. The reaction was stopped by filtration after 60 minutes and the concentration of nickel remaining in the filtrate determined by atomic absorption.

The reaction was repeated with decreasing amounts of bipy solution being added. 8.7ml (8.7×10^{-5}mol) and 3.5ml (3.5×10^{-5}mol) were added to separate reactions, giving Ni^{2+}:bipy ratios of 200:1 and 500:1 respectively.

The results are shown in **Table 3.24**.

Table 3.24

Ni^{2+}:bipy ratio	**Initial pH**	**Time /min**	**pH**	**Nickel concentration /ppm**	**% nickel removed**
100:1	4.02	30	8.43	935	9
		60	8.43	940	8
200:1	4.02	30	8.48	950	7
		60	8.47	930	9
500:1	3.99	30	8.63	958	6
		60	8.61	835	9

3.4.4 Reactions at High Temperatures.

100ml of 10,600ppm Ni^{2+} solution (1.81×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1060ppm (1.81×10^{-2}M). The pH of this solution was recorded. The solution was then heated to 75°C. 75.0ml of Neutramag slurry (2.75×10^{-2}mol) were added to the solution, giving a 60% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of nickel remaining in the filtrate determined by atomic absorption.

The reaction was repeated with the addition of 10.0ml of PPh_3 solution (1.70×10^{-6}mol), giving a Ni^{2+}:PPh_3 ratio of 10,000:1. The reaction was again repeated using a smaller excess of Neutramag, 10ml (1.81×10^{-2}mol), giving a 6% excess.

The results are shown in **Table 3.25**.

Table 3.25

% excess Neutramag used	Ligand	Time /min	Final pH	Final Ni^{2+} concentration /ppm	% Ni^{2+} removed
60	NONE	130	6.58	140	86.0
60	PPh_3	240	8.11	12	98.8
6	PPh_3	90	7.17	500	50.0

3.5 Zinc.

Another common metal ion is Zn^{2+}. It is often found in discharges from galvanising works.

The discussion for this section can be found in **section 3.8.5**.

3.5.1 Preparation of Standard Zn^{2+} Solution.

A standard concentrated solution of 10,000ppm zinc was prepared by dissolving 45.50g of $Zn(NO_3)_2.6H_20$ in 1000ml of demineralised water. This solution is equivalent to 1.53×10^{-1}M Zn^{2+}. 1ml of this solution was taken and diluted into 100ml. 1ml of this diluted solution was taken and diluted again into 100ml to give a solution of approximately 1ppm. This solution was then analysed using atomic absorption to obtain an accurate concentration of 1.00ppm. The stock solution was therefore 10,000ppm.

3.5.2 Reactions with No Ligands.

3.5.2.1 Reaction With 100ppm Zn^{2+}.

10ml of 10,000ppm Zn^{2+} solution (1.53×10^{-3}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Zn^{2+} concentration of 100ppm (1.53×10^{-3}M). The pH of this solution was recorded. 1.0ml of Neutramag slurry (1.67×10^{-3}mol) was added to the solution, giving a 10% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of zinc remaining in the filtrate determined by atomic absorption.

The results are shown in **Table 3.26**.

Table 3.26

% excess of Neutramag added	Ligand added	Initial pH	Final pH	Time /min	Final zinc concentration /ppm	% zinc removed
10	NONE	4.57	7.79	130	94	15

3.5.2.2 Reaction With 1000ppm Zn^{2+}.

100ml of 10,000ppm Zn^{2+} solution (1.53×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Zn^{2+} concentration of 1000ppm (1.53×10^{-2}M). The pH of this solution was recorded. 8.0ml of Neutramag slurry (1.68×10^{-2}mol) were added to the solution, giving a 10% excess over that needed for full stoichiometric reaction. The solution was filtered after 30 minutes and the concentration of zinc remaining in the filtrate determined by atomic absorption.

This reaction was repeated, leaving it to react for 60 minutes and 140 minutes.

The results are shown in **Table 3.27**.

Table 3.27

% excess Neutramag added	Initial pH	Final pH	Time /min	Final zinc concentration /ppm	% zinc removed
10	4.37	7.24	30	920	8
10	4.37	7.26	60	870	13
10	4.75	7.08	140	790	21

3.5.3 Reactions with Ligands.

100ml of 10,000ppm Zn^{2+} solution (1.53×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Zn^{2+} concentration of 1000ppm (1.53×10^{-2}M). The pH of this solution was recorded. 6.1ml of PPh_3 solution (6.1×10^{-5}mol) were added, giving a Zn^{2+}:PPh_3 ratio of 250:1. 10.0ml of Neutramag slurry (1.67×10^{-2}mol) were added to the solution, giving a 10% excess over that needed for full stoichiometric reaction. The reaction was filtered after 30 minutes and the concentration of zinc remaining in the filtrate determined by atomic absorption.

The reaction was repeated, leaving it to react for 60 minutes and 195 minutes. The latter reaction had a Zn^{2+}:PPh_3 ratio of 100:1 with 10ml of PPh_3 solution (1.6×10^{-4}mol) added.

A further reaction with 10.0ml of bipy solution (1.6×10^{-4}mol), giving a Zn^{2+}:bipy ratio of 100:1, was performed for 2 hours.

The results are shown in **Table 3.28**.

Table 3.28

Ligand added	Initial pH	Final pH	Time /min	Final zinc concentration /ppm	% zinc removed
PPh_3	4.26	7.18	30	900	10
PPh_3	4.26	7.18	60	890	11
PPh_3	4.71	7.09	195	690	31
Bipy	4.64	7.08	120	810	19

3.5.4 Reactions Over 4 Hours.

100ml of 10,000ppm Zn^{2+} solution (1.53×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Zn^{2+} concentration of 1000ppm (1.53×10^{-2}M). The pH of this solution was recorded. 10.0ml of Neutramag slurry (1.67×10^{-2}mol) were added to the solution, giving a 10% excess over that needed for full stoichiometric reaction. The reaction was filtered after 240 minutes and the concentration of zinc remaining in the filtrate determined by atomic absorption.

The reaction was repeated with the addition of 10.0ml TMEDA and bipy solutions, (1.6×10^{-4}mol), giving Zn^{2+}:L ratios of 100:1.

The results are shown in **Table 3.29**.

Table 3.29

Ligand added	**Initial pH**	**Final pH**	**Time /min**	**Final zinc concentration /ppm**	**% zinc removed**
None	4.26	7.18	240	620	38
TMEDA	4.71	7.09	240	580	42
Bipy	4.64	7.08	240	520	48

3.6 Lead.

3.6.1 Preparation of Standard Pb^{2+} Solution.

A standard concentrated solution of lead was made up to approximately 10,000ppm, by dissolving 15.99g of $Pb(NO_3)_2$ in 1000ml of demineralised water. This solution is equivalent to 4.83×10^{-4}M Pb^{2+}. 1ml of this solution was taken and diluted down 100 times. 1ml of this diluted solution was diluted again into 100ml to give a solution of approximately 1ppm. This solution was then analysed using atomic absorption to obtain an accurate concentration of 1.02ppm. The stock solution was therefore 10,200ppm.

3.6.2 Reactions With 100ppm Lead Solutions.

10ml of 10,200ppm Pb^{2+} solution (4.92×10^{-4}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Pb^{2+} concentration of 102ppm (4.92×10^{-4}M). The pH of this solution was recorded. 1.0ml of Neutramag slurry (6.60×10^{-4}mol) was added to the solution, giving a 35% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of lead remaining in the filtrate determined by atomic absorption.

This reaction was repeated with the addition of aliquots of various ligand solutions . 0.3ml of PPh_3, TMEDA and bipy solutions (1.79×10^{-4}mol) were used, giving Pb^{2+}:L ratios of 100:1.

The results are shown in **Table 3.30**.

Table 3.30

% excess of Neutramag used	Ligand added	Initial pH	Final pH	Time /min	Final lead concentration /ppm	% lead removed
34	NONE	5.09	6.23	40	42	58
36	PPh_3	5.20	6.46	40	42	58
36	TMEDA	5.74	6.43	30	46	54
36	Bipy	5.45	6.42	30	44	56

3.6.3 Reactions Using 1000ppm Solutions.

100ml of 10,200ppm Pb^{2+} solution (4.92×10^{-3}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Pb^{2+} concentration of 1020ppm (4.92×10^{-3}M). The pH of this solution was recorded. 10.0ml of Neutramag slurry (6.60×10^{-3}mol) were added to the solution, giving a 35% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of lead remaining in the filtrate determined by atomic absorption.

This reaction was repeated with the addition of aliquots of various ligand solutions. 0.3ml of PPh_3, DPPE, bipy, and TMEDA solutions (1.79×10^{-4}mol) were used giving Pb^{2+}:L ratios of 100:1. A further reaction with TMEDA was carried out using 3.0ml of ligand solution (1.79×10^{-3}mol) giving a Pb^{2+}:L ratio of 10:1.

The results are shown in **Table 3.31**.

Table 3.31

Ligand added	**Pb^{2+}:L ratio**	**Initial pH**	**Final pH**	**Time /min**	**Final lead concentration /ppm**	**% lead removed**
NONE	0	4.92	7.20	160	310	69
PPh_3	100:1	4.96	7.28	160	360	64
DPPE	100:1	4.90	7.24	170	380	62
Bipy	100:1	4.98	7.18	160	420	58
TMEDA	100:1	5.04	7.21	155	310	69
TMEDA	10:1	4.93	7.21	180	290	71

3.7 Aluminium

3.7.1 Preparation of Standard Al^{3+} Solution.

A standard concentrated solution of 10,000ppm aluminium was prepared by dissolving 139.00g of $Al(NO_3)_3.9H_2O$ or 123.50g of $Al_2(SO_4)_3.18H_2O$ in 1000ml of demineralised water. These solutions are equivalent to $3.70\times10^{-1}M$ Al^{3+}. 1ml of these solutions was taken and diluted into 100ml. 1ml of these diluted solutions were taken and diluted again into 100ml to give solutions of approximately 1ppm. These solutions were then analysed using atomic absorption to obtain accurate concentrations of 1.00ppm. The stock solutions were therefore 10,000ppm.

3.7.2 Reactions Using 100ppm Solutions.

10ml of 10,000ppm $Al(NO_3)_3$ solution (3.71×10^{-3}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Al^{3+} concentration of 100ppm ($3.71\times10^{-3}M$). The pH of this solution was recorded. 6.0ml of Neutramag slurry (8.24×10^{-3}mol) were added to the solution, giving a 50% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentration of aluminium remaining in the filtrate determined by atomic absorption.

The reaction was repeated with the addition of PPh_3 solution. 3.7ml of PPh_3 solution (3.71×10^{-5}mol) were added, giving an $Al^{3+}:PPh_3$ ratio of 100:1.

The results are shown in **Table 3.32**.

Table 3.32

% excess of Neutramag used	Ligand added	Initial pH	Final pH	Time /min	Final aluminium concentration /ppm	% aluminium removed
50	None	3.30	5.56	180	86	14
50	PPh_3	3.66	5.58	200	81	19

3.7.3 Reactions Using 1000ppm Solutions

3.7.3.1 Reactions Using Various Aluminium Sources.

100ml of 10,000ppm $Al(NO_3)_3$ solution (3.71×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Al^{3+} concentration of 1000ppm (3.71×10^{-2}M). The pH of this solution was recorded. 29.0ml of Neutramag slurry (6.11×10^{-2}mol) were added to the solution, giving a 10% excess over that needed for full stoichiometric reaction. A sample of the reaction mixture, approximately 80ml, was taken after 30 minutes and filtered to stop further reaction. The reaction was stopped after 60 minutes by filtration and the concentration of aluminium remaining in the filtrate determined by atomic absorption.

The reaction was repeated using an aluminium solution composed of dissolved $Al_2(SO_4)_3$.

The results are shown in **Table 3.33**.

Table 3.33

Salt used	% excess of Neutramag used	Time /min	pH	Aluminium concentration /ppm	% aluminium removed
$Al(NO_3)_3$	10	0	3.23	1000	0
		30	5.60	970	3
		60	5.61	920	8
$Al_2(SO_4)_3$	10	0	3.79	1000	0
		30	7.60	0.1	99.99
		60	7.69	0.2	99.99

3.7.3.2 Reactions with Acids Present.

50ml of 10,000ppm $Al(NO_3)_3$ solution (1.85×10^{-2}mol) were taken and 11.1ml of H_2SO_4 (5.55×10^{-2}mol) were added. This solution was diluted to a volume of 500ml with deionised water. This gave an initial Al^{3+} concentration of 1000ppm (1.85×10^{-2}M). The pH of this solution was recorded. 32.7ml of Neutramag slurry (8.61×10^{-2}mol) were added to the solution, giving a 10% excess over that needed for full stoichiometric reaction. A sample of the reaction mixture, approximately 80ml, was taken after 30 minutes and filtered to stop further reaction. The reaction was stopped after 60 minutes by filtration and the concentration of aluminium remaining in the filtrate determined by atomic absorption.

The reaction was repeated using 50ml of $Al_2(SO_4)_3$ solution (1.85×10^{-2}mol) and 27.9ml of HNO_3 (2.78×10^{-2}mol). 16.9ml of Neutramag suspension (4.44×10^{-2}mol) were added, giving a 10% excess over that needed for full stoichiometric reaction.

The results are shown in **Table 3.34**.

Table 3.34

Salt used	% excess of Neutramag used	Time /min	pH	Aluminium concentration /ppm	% aluminium removed
$Al(NO_3)_3$ + H_2SO_4	10	0	0.64	1000	0
		30	8.22	0.0	100
		60	8.25	0.0	100
$Al_2(SO_4)_3$ + HNO_3	10	0	1.27	1000	0
		30	8.36	0.0	100
		60	8.41	0.0	100

3.8 Discussion.

3.8.1 Copper

It was already known that Cu^{2+} was an easily treated metal ion. The K_{SP} of $Cu(OH)_2$ is $1.6\times10^{-19}mol^3dm^{-9}$ [8] and previous work had shown little difficulty in obtaining full precipitation, **section 1.3**. Looking at the reactions of copper was mainly of interest as it was the major constituent in an effluent which Britmag were having trouble in treating, **sections 3.2** and **3.8.2**, and so hopefully some insight could be gained by looking at the simple Cu^{2+} system. With this in mind, most of the reactions were performed with an initial Cu^{2+} concentration of just 100ppm, as the industrial effluent contained copper in just 50ppm concentration.

3.8.1.1 Reactions with High Excess of Neutramag.

Treatment of Cu^{2+} solution with a 75% excess of Neutramag gave very good results, 99.7% being removed after half an hour, **section 3.1.2.1**. This fitted in well with the previous work done by Britmag on copper systems. The addition of PPh_3 to the reaction, **section 3.1.2.2**, made negligible difference, 99.9% being removed after half an hour. There was, therefore, no real benefit to be gained by adding the ligand.,

3.8.1.2 Reactions with Lower Excesses of Neutramag.

3.8.1.2.1 Reaction with No Ligand.

The 75% excess was too large to be used in an industrial process and had been shown to be unnecessary, so the next step was to see if similar metal ion removals could be achieved with smaller excesses. The level of Neutramag was reduced to a 15% excess, which is not an uncommon excess used in industry. Reacting for an hour, **section 3.1.3.1**, all the Cu^{2+} had been precipitated, showing that there was some deterioration in the rate of reaction but acceptable concentrations could still be reached.

3.8.1.2.2 Reaction with PPh_3.

The reaction was repeated in the presence of PPh_3, and showed an interesting result, **section 3.1.3.2**. While there was little change in the removal of Cu^{2+} ions from solutions with lower levels of ligand present, as the relative amount of PPh_3 increased, the amount of Cu^{2+} removed from solution decreased, **Figure 3.1**. Rather than increasing the rate and metal ion removal as hoped, this lengthened the time necessary to precipitate down to discharge levels from 1 to 3 hours.

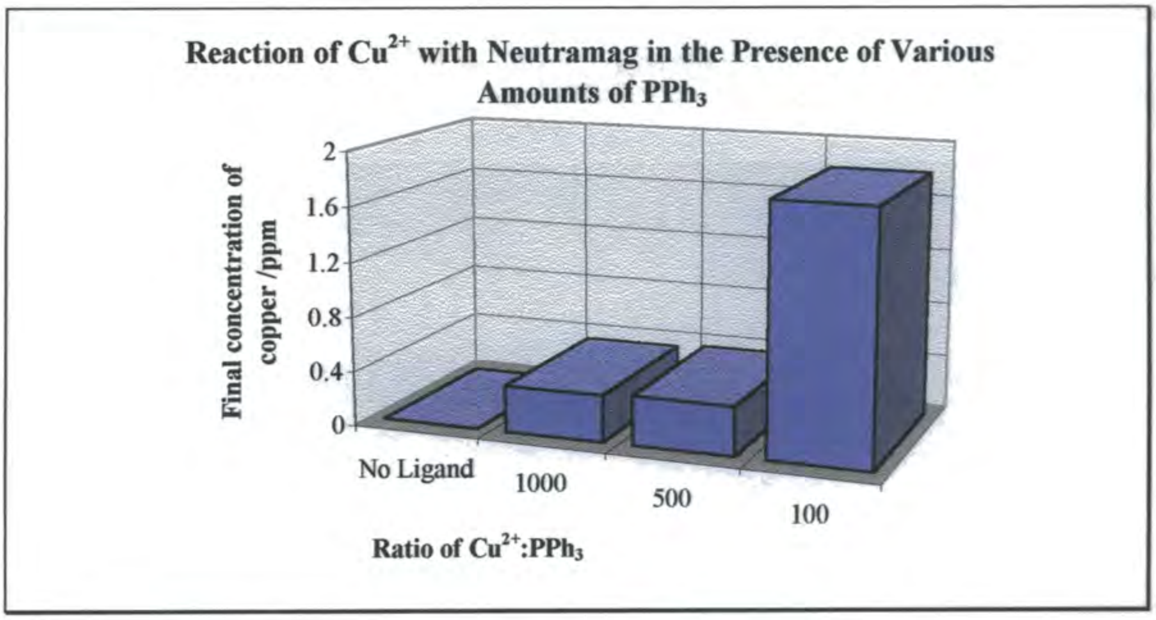
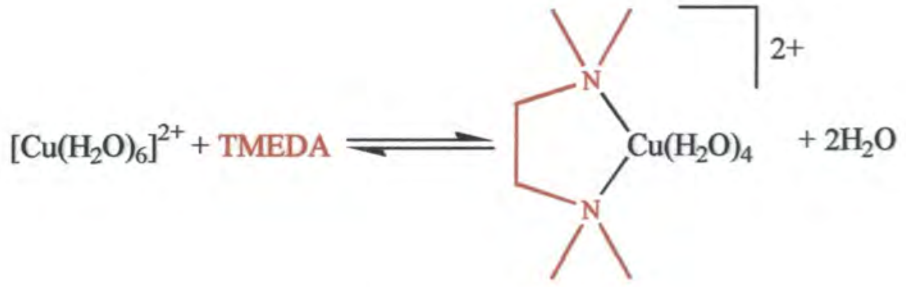


Figure 3.1

3.8.1.2.3 Reactions with TMEDA.

The ligand was changed to TMEDA and a similar set of reactions run, **section 3.1.3.3**. 10:1, 100:1 and 1000:1 Cu^{2+}:TMEDA ratios were used and the detrimental effect of the ligand was again seen. The higher the concentration of TMEDA in the reaction, the lower the metal ion removal, **Figure 3.2**.

Figure 3.2 also shows that in the 10% addition of TMEDA (10:1 Cu^{2+}:TMEDA) there is a 10% decrease in removal, 1% addition (100:1 Cu^{2+}:TMEDA) gives a 1% decrease in removal and there is little difference in the 0.1% (1000:1 Cu^{2+}:TMEDA) reaction, compared with no addition of any ligand. This seemed to indicate that there was a stoichiometric side reaction occurring, the reaction shown in **Equation 3.1** seems to be the most likely.



Equation 3.1

The 10% TMEDA solution was visibly blue after filtration, indicating that there were still plenty of copper ions left in solution.

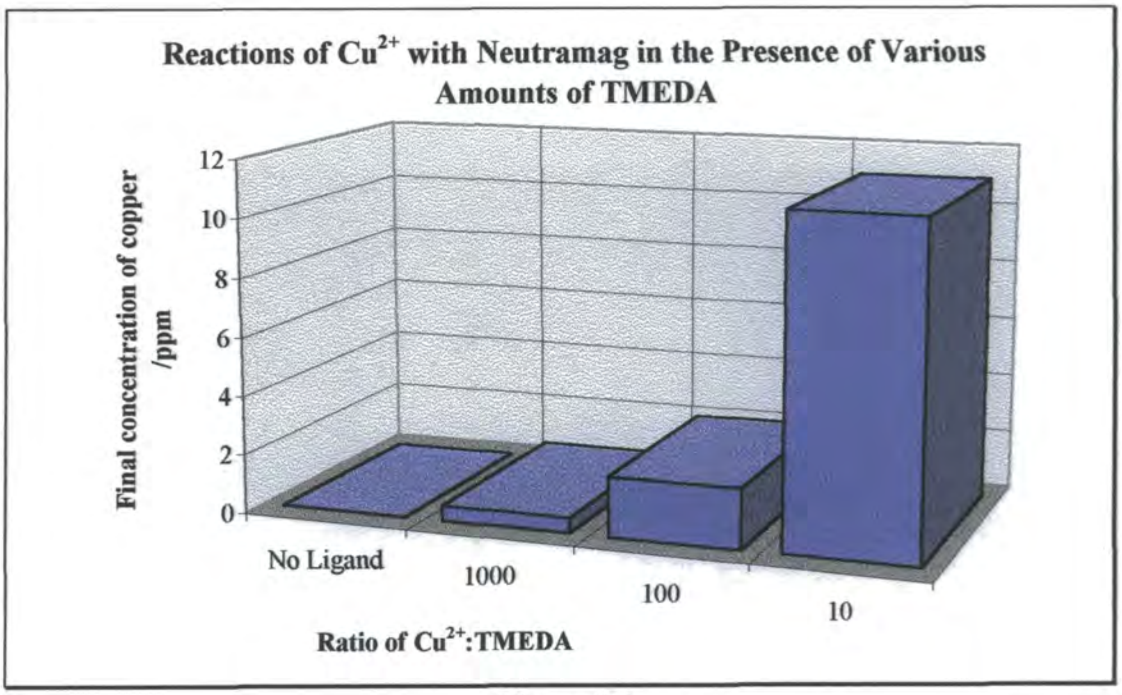

Reactions of Cu^{2+} with Neutramag in the Presence of Various Amounts of TMEDA

Figure 3.2

3.8.1.2.4 Reactions with Other Chelating Ligands.

Other chelating ligands were tried to see if they had the same effect on the reactions, **section 3.1.3.4**. DPPE gave very poor results; a 1% solution (100:1 Cu^{2+}:DPPE) decreased the metal ion removal by 10% after 90 minutes. This seemed odd when compared to the oither ligand results. It would seem to indicate either a very erroneous result or a different reaction was occurring. Bipy, which is a weaker donor, did not affect the reaction any more than TMEDA did, a 1% solution decreasing the metal ion removal by approximately 1%, giving the same stoichiometric results.

3.8.1.3 Reactions at Higher Concentration.

A reaction was performed at higher concentrations, **section 3.1.4**, to check that the results were valid for stronger effluent systems. The reaction was completed in just 16 minutes, giving a very similar concentration to the previous reactions even though it started from 10× the initial concentration.

3.8.1.4 Summary.

The data collected from these reactions showed an order for increasing copper precipitation as shown in **Figure 3.3**.

$$\text{DPPE} < \text{PPh}_3 < \text{TMEDA} < \text{bipy} < \text{no ligand}$$

Figure 3.3 Trend For Increasing Removal of Cu^{2+}

These results were the reverse of those obtained, both previously and later in this project, for solutions high in iron and zinc. It follows that as the strength of the metal-ligand bond increases, the amount of precipitation decreases, as opposed to reactions in the iron systems previously observed, where a catalytic effect was seen due to the ligand being displaced from the metal complex

This seemed to indicate that, as opposed to the reactions where a catalytic effect was occurring due to the ligand being displaced from the metal complex, allowing it to precipitate as the hydroxide, the ligand was in fact bonding permanently to the metal centre. This would produce a more stable complex which could be more soluble in aqueous solution. The stronger the bond between metal and ligand, the less likely it is to be exchanged by a water molecule or hydroxide ion for the catalytic process to continue.

This idea corresponds to the Irving-Williams order for transition metal(II) complexes, **Figure 3.4** [17].

$$\mathrm{Mn^{II}} < \mathrm{Fe^{II}} < \mathrm{Co^{II}} < \mathrm{Ni^{II}} < \mathrm{Cu^{II}} > \mathrm{Zn^{II}}$$

Figure 3.4 Irving-Williams Order

On going from left to right across the periodic table, the bonds between metal and ligand in a complex increase in strength. This is due to the contraction of ionic radii across the period, and hence decreasing the M-L distance. This would seem to indicate that zinc should form the strongest bonds. This is not the case, however. Copper forms stronger bonds than zinc due to a higher Crystal Field Stabilisation Energy (CFSE) †.

The reaction between ligand and copper seems to be in a 1:1 ratio. Approximately a 1% decrease in metal ion removal is seen for 100:1 ratios, 10% decrease for 10:1 ratios etc.. There seems to be little difference between the uni- and bi-dentate ligands. The bonding of just 1 ligand per copper centre was apparently enough to keep the metal ion in solution at the pHs obtainable with Neutramag.

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† As ligands are brought closer to a metal centre, the electrostatic field which is produced splits the degenerate d-orbitals to higher or lower energies, depending on their symmetries. These orbitals then allow the system to be at a lower energy, depending on the number of electrons present. Cu^{2+} has a d^9 configuration which gives it $^3/_5\Delta_o$ CFSE in an octahedral complex. Zn^{2+} has a d^{10} configuration, thus not gaining anything from CFSE and so bonding less strongly with the ligands. Cu^{2+} also gains from the Jahn-Teller Effect, which causes degenerate orbitals containing electrons to split allowing a lower energy state to be achieved.

This property could make the treatment of effluents containing high concentrations of both copper and donating species, or a metal which is co-treated with a donor ligand, much more difficult with Neutramag.

An interesting observation in these reactions was a small hump in the pH profiles. On first addition of the Neutramag, the pH increased sharply as expected, before slowing down. The pH then started to decrease for a few minutes before increasing again with the reaction carrying on as expected.

The first, quick increase was probably due to the copper and hydroxonium ions reacting with the hydroxide already in solution. This would be a quick process, as copper hydroxide has been seen to have a very low solubility product. The system would then have to wait for more hydroxide to dissolve before any further precipitation could occur. This would explain the slowing of the increase in pH. It is possible, however, that copper is so insoluble that it extracts hydroxide from the water solvent to continue precipitation, leaving hydroxonium ions which would cause the pH of the solution to go down, .

e.g.

Table 3.35

Time /min	0	1	2	3	4	5	6	7	9	10	12	14	16	18	20	25	45	50
pH	4.30	5.15	5.27	5.33	5.24	5.15	5.15	5.16	5.20	5.23	5.29	5.37	5.45	5.54	5.64	5.89	7.55	8.21

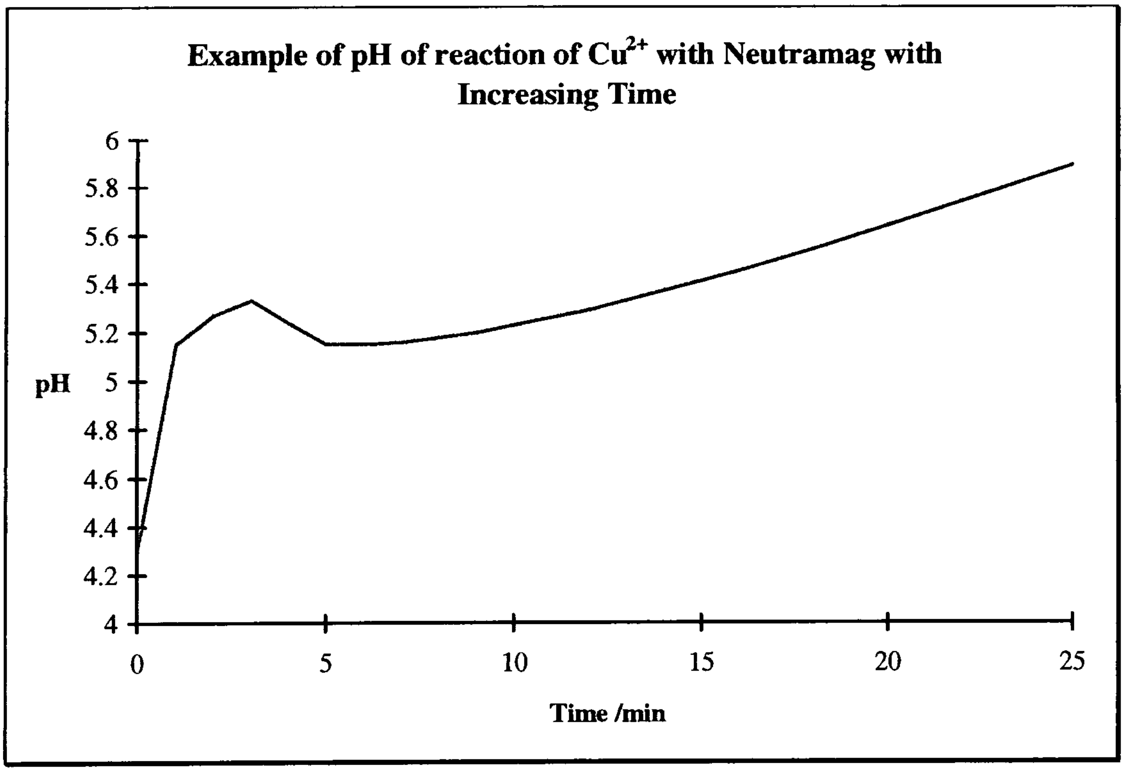

Figure 3.5

$$[Cu(H_2O)_6]^{2+} + OH^- \longrightarrow [Cu(H_2O)_5OH]^+ + H_2O$$

$$[Cu(H_2O)_5OH]^+ + H_2O \longrightarrow Cu(OH)_2 + 5H_2O + H^+$$

Figure 3.6 Proton Abstraction and Precipitation of Cu^{2+} with Low Concentration of OH^-

3.8.2 Industrial Sample.

3.8.2.1 Introduction.

The next solution tested was an actual effluent from a printed circuit board manufacturer, which contained copper as the main metal ion present. Ordinarily this would not be expected to be a problem in treatment with Neutramag, **section 3.1** and **section 3.8.1**, but complete removal of the copper ions proved to be very difficult. A study of the effluent with various ligands seemed appropriate to see if any improvement could be made.

Having a problem removing copper from an effluent was unusual. The main problem seemed to be that the solution also contained high concentrations of ammonium ions from one of the production processes. It was thought that it was these ions which were causing the difficulty in removal of the copper.

The raw effluent did not contain a high concentration of metal ions compared to some solutions that are treated industrially, only approximately 50ppm of copper ions being present. Although this is quite low it still requires further treatment before it can be safely discharged. As there was only a limited amount of effluent available to study, it was decided to dilute it by 10 times to give enough solution to work with. This meant that the solutions used for most of the reactions were only approximately 5ppm in copper, although this was still enough to observe any changes in the reactions.

The presence of ammonium ions seemed unlikely to cause many problems to the precipitation reactions. As the pH increased with the addition of Neutramag, however, the ammonium ions would become deprotonated, leaving ammonia, pK_a of $NH_4^+ = 9.25$. The ammonia could then bind to the copper ions. This follows from the experiments performed on copper solutions, **section 3.1** and **section 3.8.1**, where addition of donor ligand species reduced the amounts of precipitation achieved by the formation of stable, soluble complexes. Thus whereas with some metals the presence of the ammonia would be beneficial to the precipitation process, it is definitely detrimental for this sample.

3.8.2.1.1 Problems.

The reactions with the industrial sample were complicated by the fact that it contained a high concentration of acid compared to the concentration of copper which needed to be removed. A pH of 2 (1×10^{-2}M H^+) and a Cu^{2+} concentration of 50ppm (7.71×10^{-5}M) means that there are over 100 times the amount of acid than metal ions. This acid had to be neutralised for the precipitation reactions to occur. The amount of Neutramag needed to neutralise the acid was calculated from the pH of the initial reaction solution. The neutralisation of the acid did not require any excess Neutramag, however, and this led to some rather large errors in the calculation of base to be added.

e.g. 1000ml of 50ppm Cu^{2+} solution at pH 3 contains

1×10^{-3}mol of H^+ ∴ required 5.00×10^{-4}mol of Neutramag

7.71×10^{-5}mol Cu^{2+} ∴ required 7.71×10^{-5}mol of Neutramag

Total amount of Neutramag required = 5.77×10^{-4}mol

A 10% excess of this figure = 6.35×10^{-4}mol

A 10% excess for the Cu^{2+} only = 7.71×10^{-5}mol × 1.1

\+ 5.00×10^{-4}mol

= 5.85×10^{-4}mol

This discrepancy led to much larger excesses of Neutramag being used in these reactions than was originally intended. However, with even these excesses complete removal of the copper from solution proved impossible.

3.8.2.2 Reactions at High Excesses.

Britmag's initial work with this effluent had showed that complete precipitation could not be achieved even with quite large excesses. The first reactions performed looked at the use of large excesses of Neutramag, although they were somewhat larger than originally intended, **section 3.8.2.1.1**.

An excess of 1570%, a 15 fold excess, was tried, but even this amount of Neutramag was not enough to achieve complete precipitation, **section 3.2.2.1.1**.

To see if the addition of another donating ligand would improve the metal ion removal, reactions with PPh_3 were attempted, **section 3.2.2.1.2**. The PPh_3 did improve the metal ion removal, dropping the remaining Cu^{2+} below 1ppm. This ran contrary to the expected results as PPh_3 is a stronger ligand than NH_3 and, as was seen with the simple Cu^{2+} solutions, **section 3.1**, was expected to decrease the reactivity. An even lower level was achieved using a larger excess of Neutramag, 4055%, and the PPh_3 ligand, **Figure 3.7**.

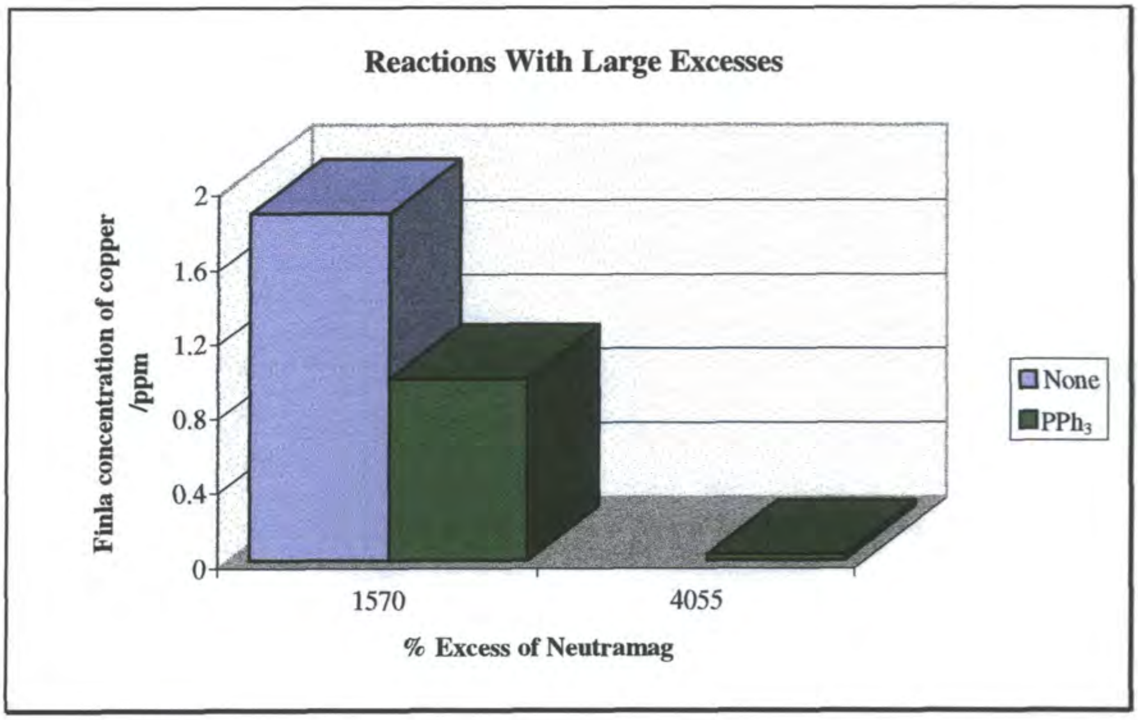

Figure 3.7

3.8.2.3 Reactions Using Lower Excesses.

These excesses were far too high to be used in industry so lower ones were tried. Although still high it was hoped that some sort of improvement would be seen for the amount of Neutramag added. Excesses of between 300% and 950% were tried, **section 3.2.2.2.1** and **Figure 3.8**. Progressively more Neutramag improved the amount of precipitation.

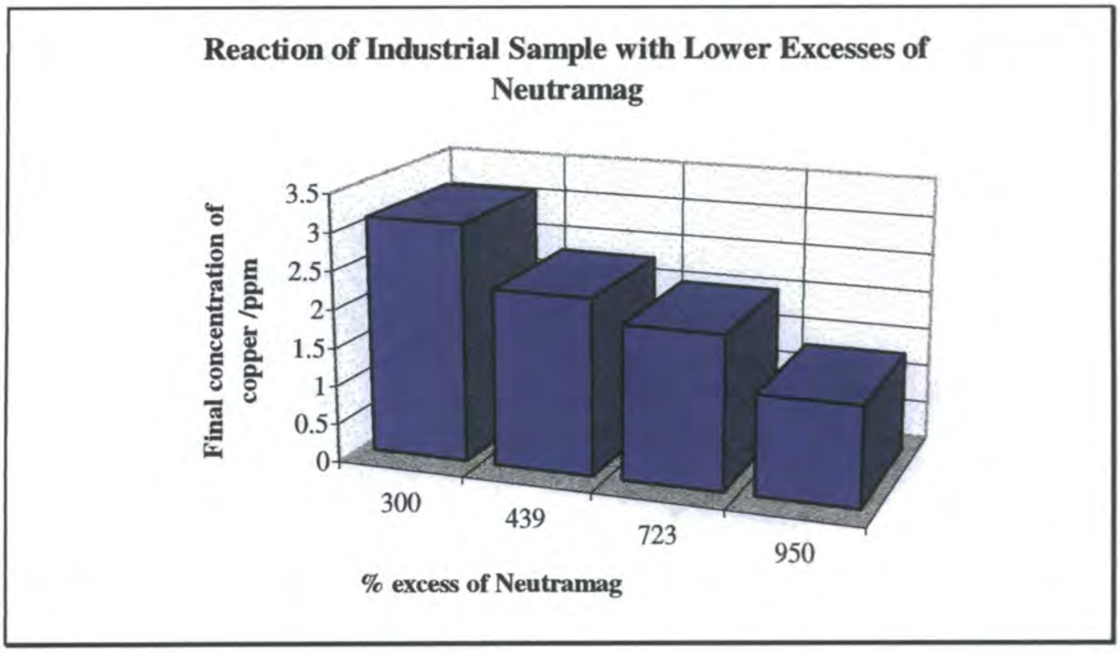

Figure 3.8

Similar reactions with PPh_3 present were also tried, **section 3.2.2.2.2**. Although the results were slightly improved over the reaction without PPh_3, increasing the amount of base added did not affect the metal ion removal greatly at the levels tested, **Figure 3.9**.

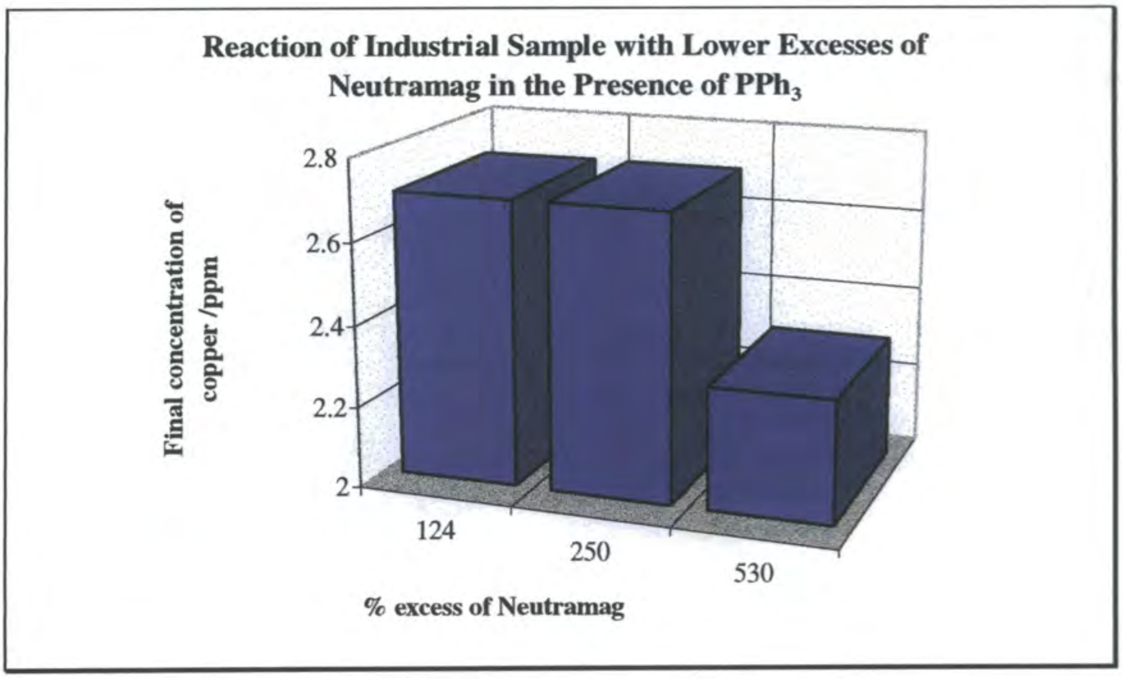

Figure 3.9

3.8.2.4 Reactions with Undiluted Solutions.

These reactions were performed on solutions which were initially very dilute. In order to give more accurate, and possibly realistic, information on the system, undiluted samples were used in reactions.

Reactions were run using 500% excesses of Neutramag with various ligands over the period of 100 minutes, **section 3.2.3.1** and **Figure 3.9**. None of the reactions showed any improvement over the others although the levels achieved were much lower than expected.

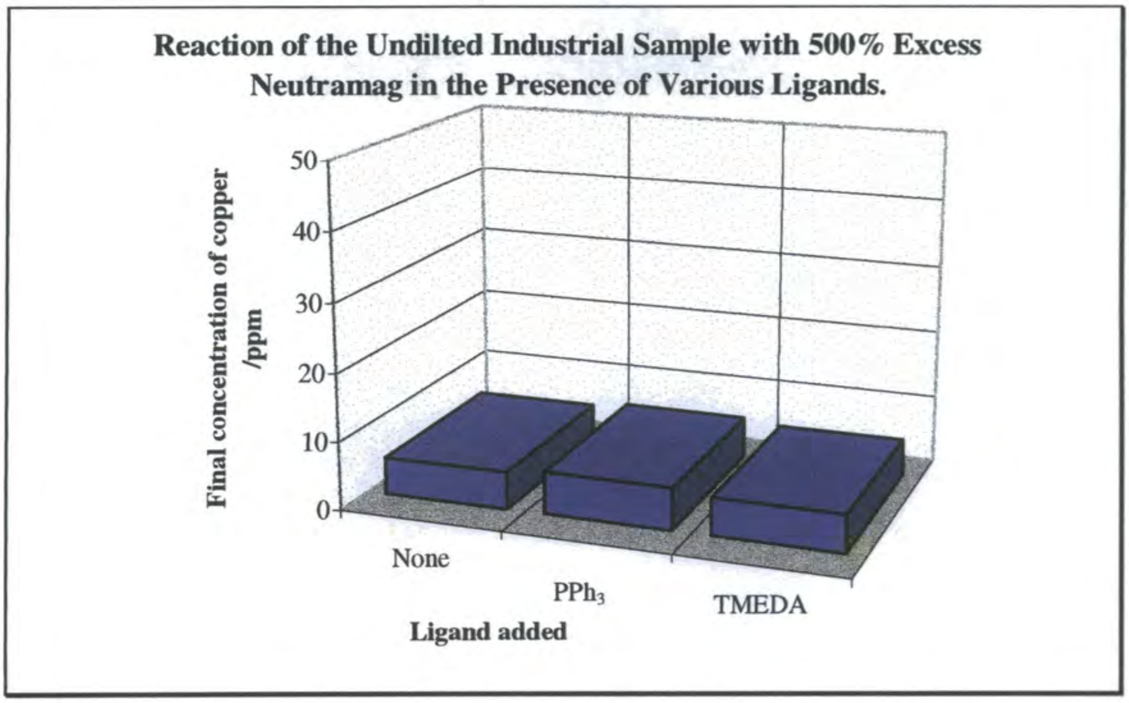

Figure 3.10

The reactions with dilute samples gave final concentrations of the same order, but started at lower concentrations, so the % removed was much lower, **Figure 3.11**.

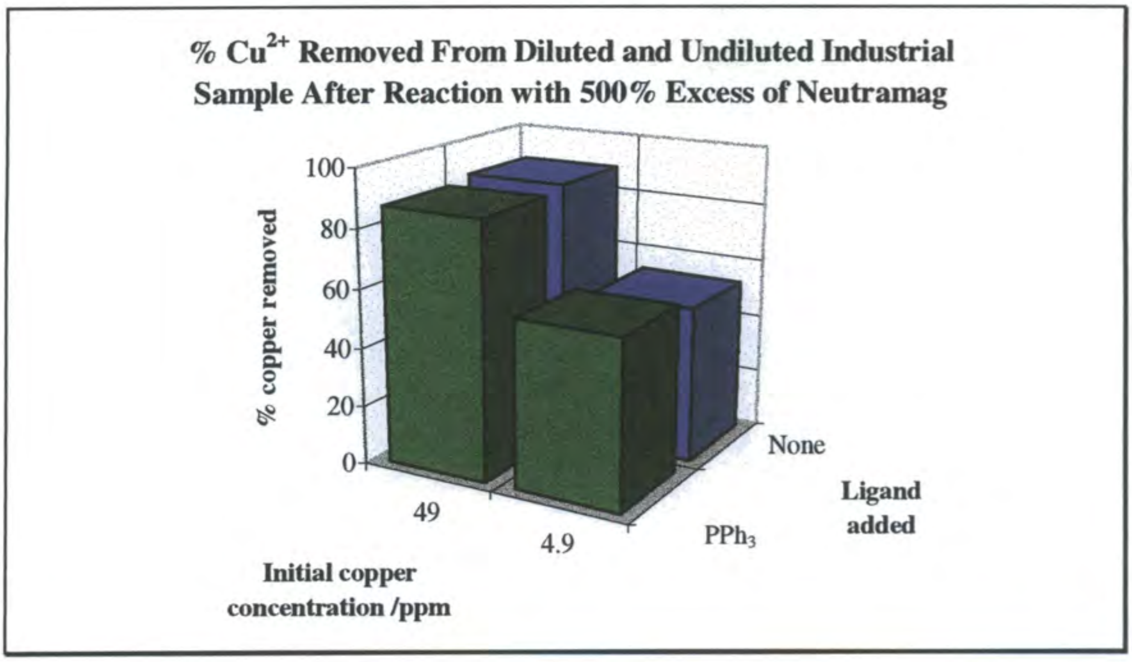

Figure 3.11

Using lower excess with no ligand decreased the % removed only slightly, **section 3.2.3.2**. Allowing the reaction to proceed for a longer period of time did improve the amount precipitated. 94% removal was an improvement on any result previously seen for this system.

This seemed to indicate that the reactions were proceeding after the time when the previous reactions had been stopped by filtration. The large excess of Neutramag may actually have worked if given long enough to react. The increasing excesses actually improve the rate of reaction rather than the absolute final stoichiometry.

In order to treat this effluent more efficiently, alternative ideas were considered. As it is the ligand, NH_3, which was causing the problem, the obvious step was its removal. This process would have to leave no chemicals in solution which were harmful, or the entire process would be rendered pointless. The removal could be achieved by oxidation of the ammonia to nitrate, NO_3^-. Using acids as oxidants would greatly increase the amount of Neutramag require for the treatment and is self-defeating. It was decided that hydrogen peroxide would be a viable, if industrially expensive, additive, as it is capable of oxidizing NH_3 to NO_3^- and would only give water and acid as by-products.

$$NH_3 + 4H_2O_2 \longrightarrow NO_3^- + H^+ + 5H_2O$$

Equation 3.2

As there was no actual effluent remaining, a synthetic solution were prepared which contained Cu^{2+} solution and ammonia, **section 3.2.3.3.1**. When the control reactions was performed, however, there seemed to be little degradation in the metal ion removals compared to normal copper reactions, **section 3.2.3.3.2**. This seemed to indicate that either the concentration of NH_3 was not high enough or that some other reaction was occurring in the effluent sample.

The reaction using the H_2O_2 solution produced an unexpected result. When the Neutramag was added to the solution, the reaction mixture quickly turned green. Black precipitate then started to form. This was almost certainly copper(II) oxide, CuO, formed from the reaction with the H_2O_2, **Equation 3.3**. There was more than enough H_2O_2 present in the solution as the Cu: H_2O_2 ratio was 1:16. This also accounts for the unusually high pH attained during the reaction, all the OH^- ions from the Neutramag contributing to the pH.

$$Cu^{2+} + H_2O_2 + 2OH^- \longrightarrow CuO + 2H_2O + \tfrac{1}{2}O_2$$

Equation 3.3

While this reaction worked well, it was still unclear as to whether it would have worked well in the normal effluent system with higher NH_3 concentrations. If the H_2O_2 reacts preferentially with the Cu^{2+} ions, then it would allow the reaction to proceed to completion and the Neutramag would only be required to remove the acid produced rather than cause any precipitation of the copper ions.

3.8.3 Iron(II)

Iron(II) is one of the most difficult metals to remove from solution and is also one of the most common. Many of the effluents treated by Redland have high $Fe^{(II)}$ content, often of the order of 10,000 ppm. These points make it probably the most important metal ion for improvements to the extraction process to be obtained. However, although sufficient $Mg(OH)_2$ is added, the solution never reaches dischargable concentrations or the pH buffer level.

The previous project made large increases in removal for $Fe^{(II)}$ rich solutions with the addition of donor ligands, the greatest benefit being achieved using PPh_3.

3.8.3.1 Aeration Reactions.

The first area examined in the studies of $Fe^{(II)}$ was the use of aeration in the reactions, **section 3.3.2**. Britmag had had some success in the use of aeration in the treatment of $Fe^{(II)}$ effluents. The air bubbling through the reaction not only increases the mixing of the reactants but also causes oxidation of the $Fe^{(II)}$ to $Fe^{(III)}$. The $Fe^{(III)}$ is much easier to precipitate, $K_{SP}(Fe(OH)_2) = 7.9\times10^{-16} mol^2dm^{-6}$; $K_{SP}(Fe(OH)_3) = 2.0\times10^{-39} mol^3dm^{-9}$ [8], although it will require more Neutramag to precipitate a trivalent ion.

Various periods of aeration were used, pre-aerating the solution before addition of the Neutramag as well as during the reaction time. The control reaction with no aeration produced a green precipitate of $Fe(OH)_2$, as expected. The aerated reactions both produced brown precipitates of $Fe(OH)_3$. Looking at the levels of Fe remaining in solution is less clear, however. The reactions were filtered and hence stopped when the pH of the mixture stopped increasing, even though this was after a short time. It can be seen, however, that even with less excess Neutramag and shorter reaction times less iron remains in solution. The reaction was repeated, this time leaving to react for 90 minutes, irrespective of the pH profile, before filtration and analysis. There was a much greater removal seen in this case.

During the reaction the pH did level off at 6.10, then actually fell to 5.03. The reason for this is the decreased solubility of the iron species. As the Fe^{2+} is oxidised, the Fe^{3+} produced is very susceptible to precipitation and, in order to maintain the solubility equilibrium, abstracts hydroxy ions from the solution water molecules, leaving hydroxonium ions and causing the pH to decrease, **Scheme 3.1**.

$$4Fe^{2+} + O_2 + 4H_3O^+ \longrightarrow 4Fe^{3+} + 3H_2O$$

$$Fe^{3+} + 6H_2O \longrightarrow Fe(OH)_3 + 3H_3O^+$$

Scheme 3.1 Oxidation of Fe^{2+}

3.8.3.2 Reactions of Fe^{2+} Using PPh_3.

The next reactions looked at the effect of donor ligands on the $Fe^{(II)}$ reactions. To test the varying reactions of iron(II) rather than iron(III), aeration of the reaction was not used. This should prevent too much of the iron being oxidised, as was seen above.

100:1 Fe:L ratios were used to get the biggest improvements without wasting additives. The gain of adding PPh_3 has been shown to level off at a ratio of approximately 80:1, **section 1.4** and **Figure 1.14**.

Simple addition of PPh_3 solution improved the removal of iron from solution by 10%, **section 3.3.3** and **Figure 3.12**. This reaction took less than 20 minutes.

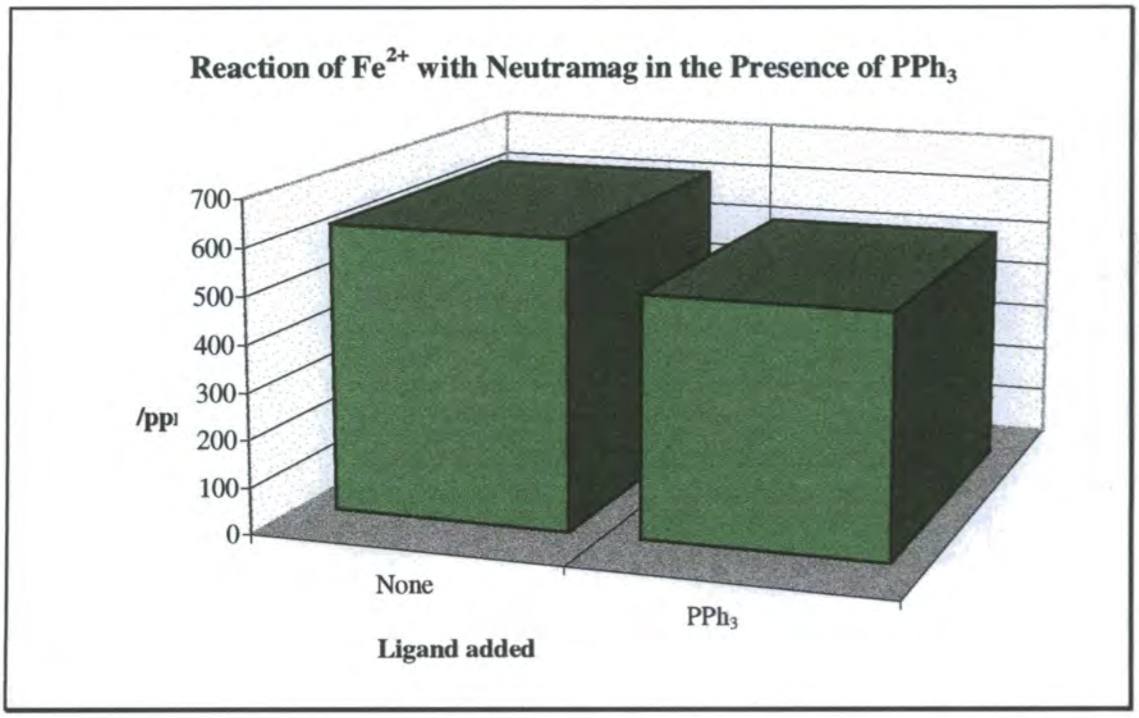

Figure 3.12

3.8.3.3 Reactions with Various Ligands.

Reactions were then performed using different ligands but keeping all other aspects of the reaction the same, **section 3.3.4**. PPh_3, TMEDA and DPPE were tested in these reactions and, as expected, the two P-donor ligands gave the greatest improvements, both removing >99.5% of the iron from solution. The N-donor ligand TMEDA also showed good improvement although not to the same level, **Figure 3.13**.

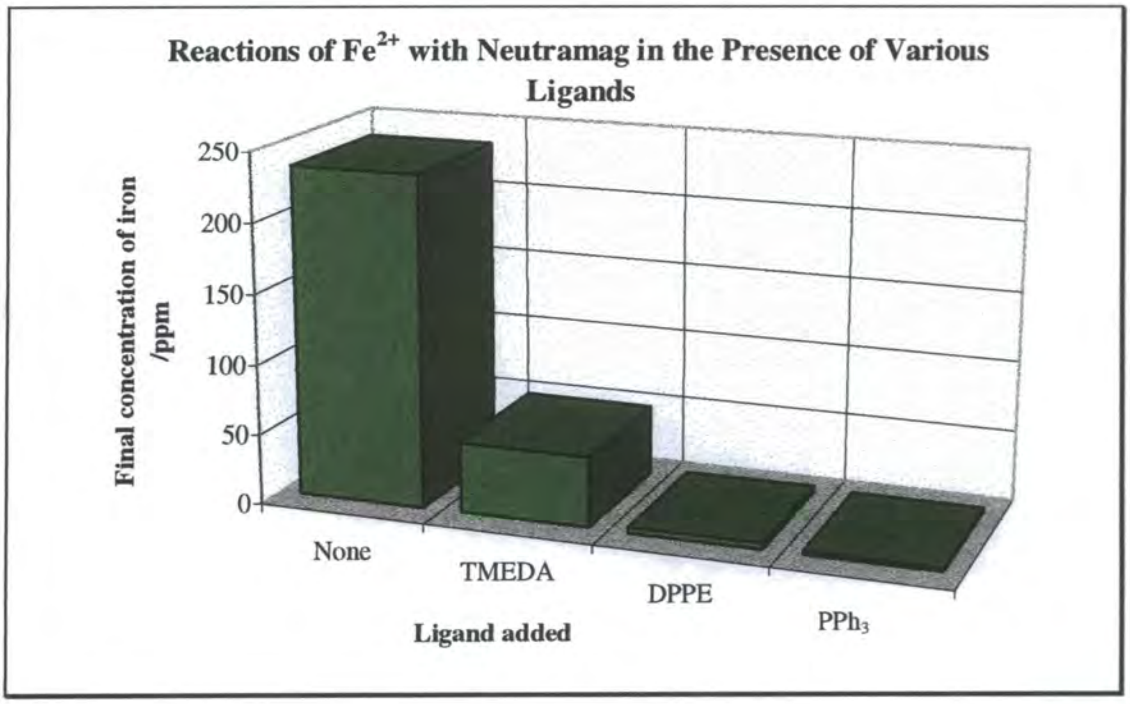

Figure 3.13

Two control reactions with no ligand present were also performed, one for 10 minutes, the other for 110 minutes. In just 10 minutes, 70% of the iron was removed from solution. Leaving the reaction for a further 100 minutes removed only a further 5%. This seemed to indicate that most of the reaction occurs very quickly, i.e. in the first 10-30 minutes, with little further precipitation occurring after this period. This was very good for industrial processes which require quick treatment of effluents, although the remaining percentage needs to be reduced further before discharge.

3.8.3.4 Summary.

It has been shown that the addition of ligands catalytically affects the reaction with iron(II). It was seen that DPPE, a ligand higher in the spectrochemical series than PPh_3, **Figure 1.11**, did not improve the reactions over the rate achieved by PPh_3. The formation constant for the Fe-DPPE complex should be larger than that for Fe-PPh_3 because of the chelate effect [18] , and cause the rate to increase. This apparently does not happen, and PPh_3 is an equally effective catalyst. Other ligands may provide better results but magnitude of the formation constant does not seem to be the answer. In any case, if the complex becomes too stable and the ligand is not displaced by H_2O or OH^-, the catalytic effect will be lost, as in the case with copper(II) discussed previously.

3.8.4 Nickel.

Nickel(II) is another metal ion that has caused many problems for Britmag, requiring the use of very large excesses of Neutramag. It is also another very common metal ion in effluents that are treated, and so it was important to improve the amount of precipitation achieved.

3.8.4.1 Reactions with No Ligands.

3.8.4.1.1 Reactions at 100ppm.

The first reactions, run using 100pppm solutions, showed the results that would become typical of nickel reactions. Less than 10% of the Ni^{2+} was removed from solution with a 47% excess, although the pH did reach 8.5, **section 3.4.2.1**. There was little change between the two times measured, **Figure 3.14**. This seems to indicate that the reaction proceeds to a certain point quite quickly, then stops with no further precipitation occurring.

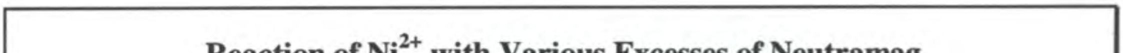

Figure 3.14

3.8.4.1.2 Reactions at 1000ppm.

Repeating these reactions with a higher initial concentration of nickel showed similar results, **section 3.4.2.2**. Although 90ppm of Ni^{2+} was removed in the half hour reaction time, this was still less than 10% of the total nickel present.

Reducing the excess of Neutramag used to just 10% again showed similar results, 7% being removed in half an hour and 10% in a further 3 hours. Again the reaction seemed to slow greatly in the latter stages. This showed very little improvement on the addition of a further 40% excess of Neutramag, **Figure 3.15**.

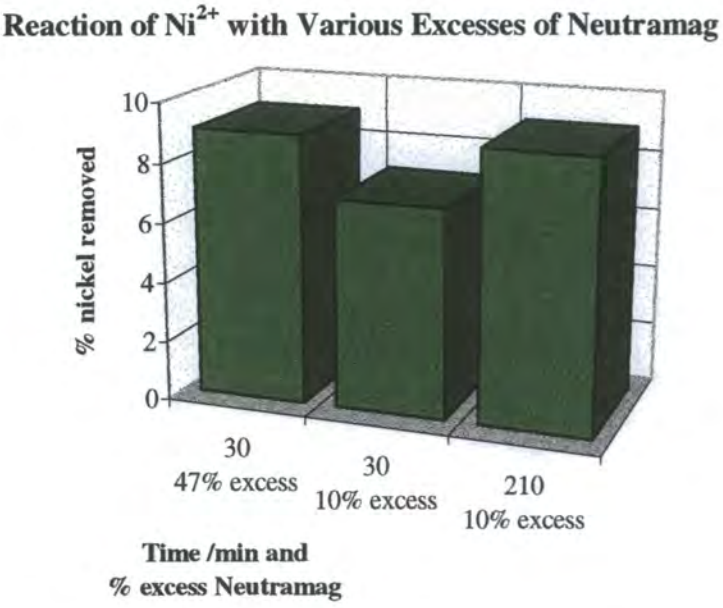

Figure 3.15

3.8.4.2 Reactions with Ligands.

The previous project had shown improvements in effluents containing large amounts of Ni^{2+}. It was hoped that the single metal systems would show the same catalytic effects with addition of donor ligands, as seen with $Fe^{(II)}$ rich solutions, **section 3.3**. The largest improvements were seen with PPh_3 so this was the first ligand to be tested.

3.8.4.2.1 Reactions with PPh$_3$.

Reactions were performed at the relatively high excesses of 50 and 60% as well as the more usual 10%. The PPh$_3$ solution was added in varying amounts to the separate reactions, giving Ni^{2+} ratios of between 100:1 to 10000:1. The 10% excess reaction showed no improvement using PPh$_3$, producing a 6% removal, **section 3.4.3.1.1**.

Increasing the excess to 60%, did show an improvement, **section 3.4.3.1.2**. The PPh$_3$ rich 100:1 reactions gave results of approximately 30% for the two times reacted, 130 and 180 minutes, **Figure 3.16**. The 10,000:1 reactions gave variable results. After 130 minutes only 15% of Ni^{2+} was removed from solution, but the metal ion removal continued to increase to 24% after 3 hours.

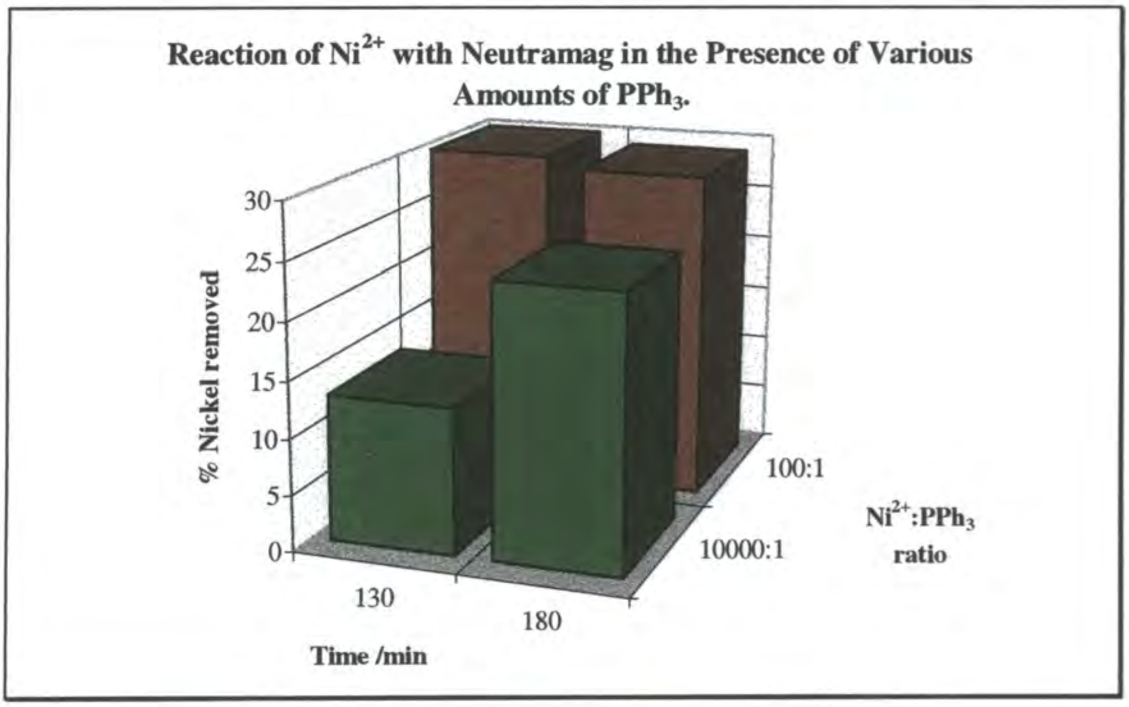

Figure 3.16

This indicated that the addition of the ligand made no difference to the final metal ion removal achieved, but did influence the rate at which this point was reached. Letting the reaction proceed for much longer showed that this did not help and no further reaction takes place.

There was no real improvement in removal of Ni^{2+} with the use of PPh_3 at any given ratio. Although there were improvements over the reaction without the ligand, no reaction removed more than 30% of the metal. These reactions are almost certainly finished as the pH has settled, and even after 21 hours there is no improvement in the amount removed.

As there was no great increase for reactions with PPh_3, different ligands were tried. TMEDA and bipy were reacted at Ni^{2+}:L ratios of 100:1, 200:1 and 500:1. For TMEDA the trend was disappointing, removing less Ni^{2+} from solution with increasing amount of ligand present, **section 3.4.3.2** and **Figure 3.17**. This may indicate that a similar process to that which occurs with Cu^{2+} is happening, but the already poor results mask the clear indications seen there.

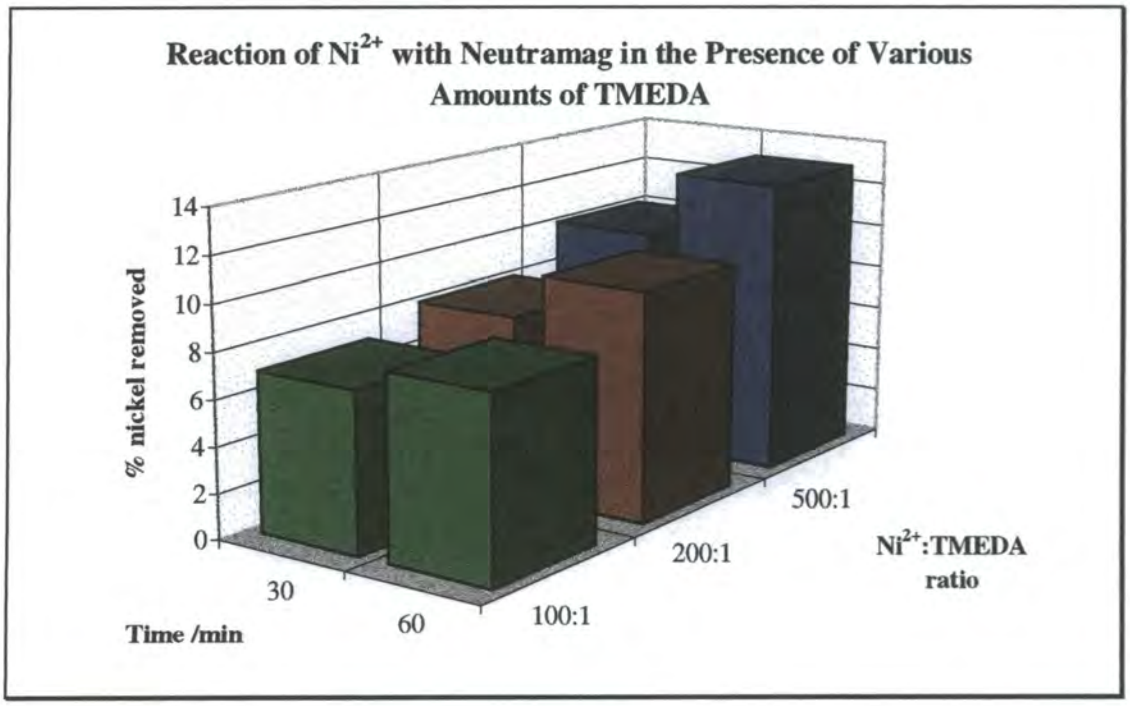

Figure 3.17

The reactions with bipy showed little difference in the amount of Ni^{2+} removed from solution, the general trend being rather inconclusive, although increasing the amount of bipy present seemed to improve the speed at which the final concentration is reached, **section 3.4.3.3** and **Figure 3.18**.

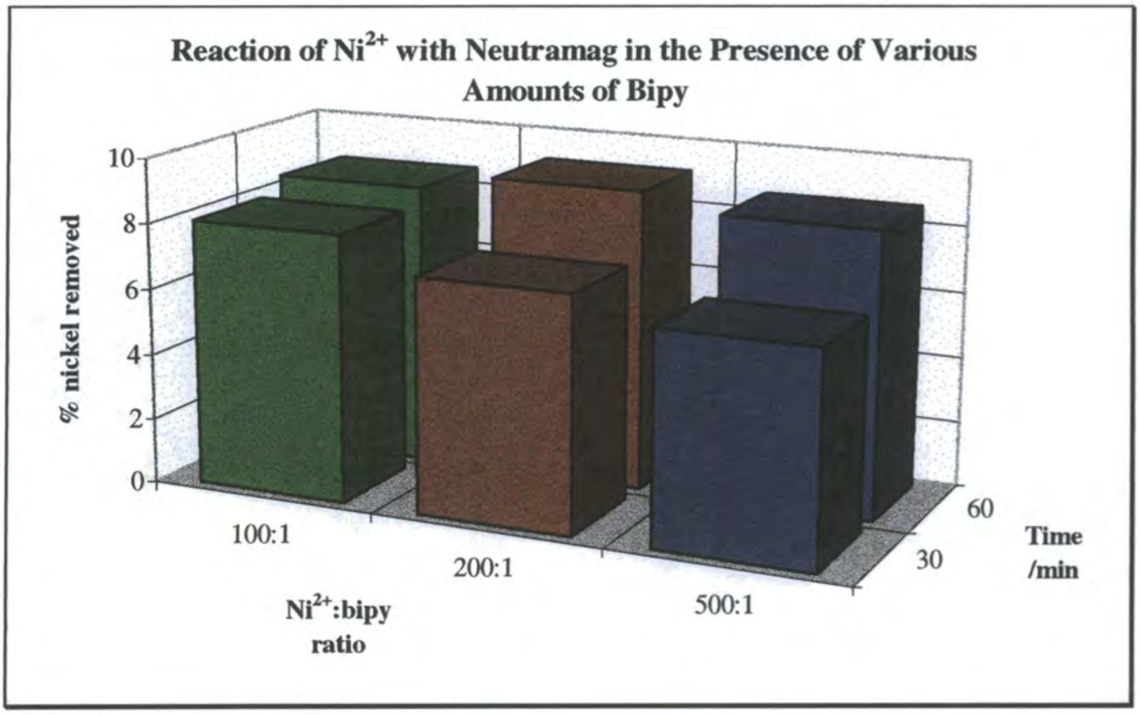

Figure 3.18

At the lower excess level of 10% there seemed to be little improvement with any of the ligands, **Figure 3.19**.

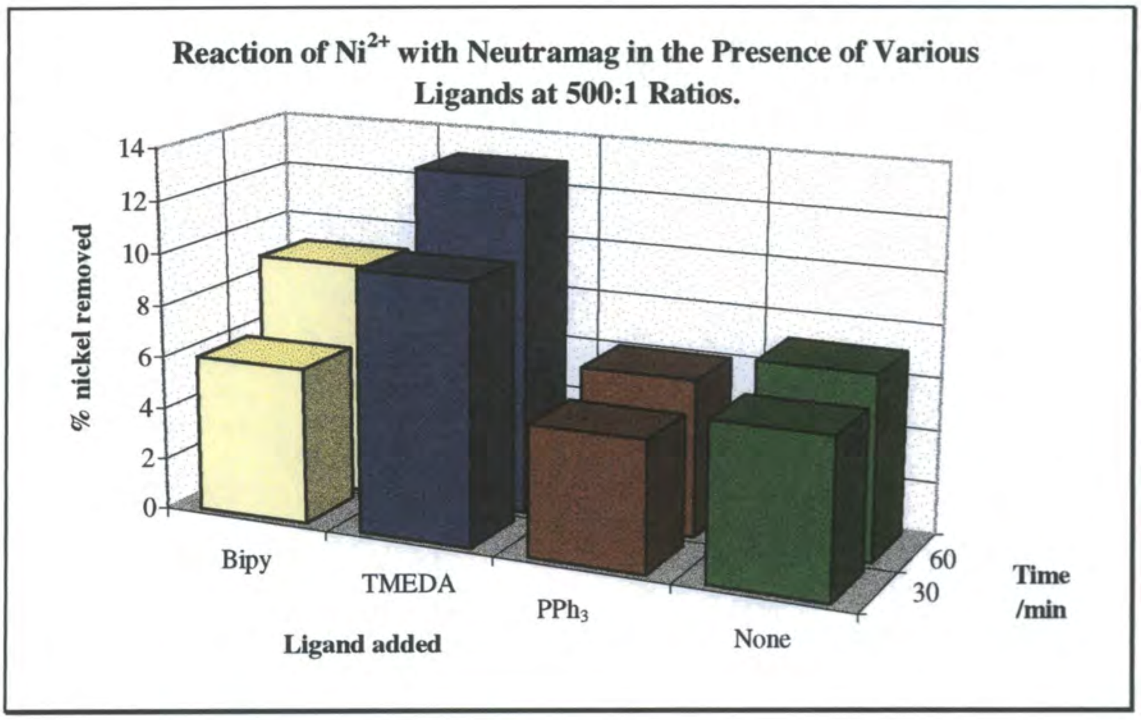

Figure 3.19

The metal ion removals for these reactions were similar to those observed previously, although in a much shorter space of time. This could mean that the reactions finish very quickly and do not proceed past the 30% mark without some further impetus. The presence of the ligand does not seem to make any difference, even to the point of making the reaction worse.

3.8.4.3 Reactions at High Temperature.

The addition of ligands did not help the reactions so more drastic steps were needed. As previously mentioned, **1.4**, increasing the temperature of the reaction by 10°C roughly doubles the rate of reaction. At higher temperatures more of the Neutramag suspension would be dissolved. This would help in the initial reaction with the $[Mg(H_2O)_6]^{2+}$ as the concentration of OH^- in solution would higher. This would also mean that there would be less solid Neutramag that could be removed from the reaction by coating and hence the reactions should proceed further.

Heating the Ni^{2+} solution to approximately 75°C prior to addition of the Neutramag was found to have a large effect on the amount of precipitation, **section 3.4.4**. In just over 2 hours 85% of the Ni^{2+} was removed from solution using just a 60% excess of Neutramag. This was a vast improvement and so the reaction was repeated with the addition of PPh_3. This gave very high removal of Ni^{2+}, 98.8%, as did the reaction with just 6% excess of Neutramag, which gave a 50% removal.

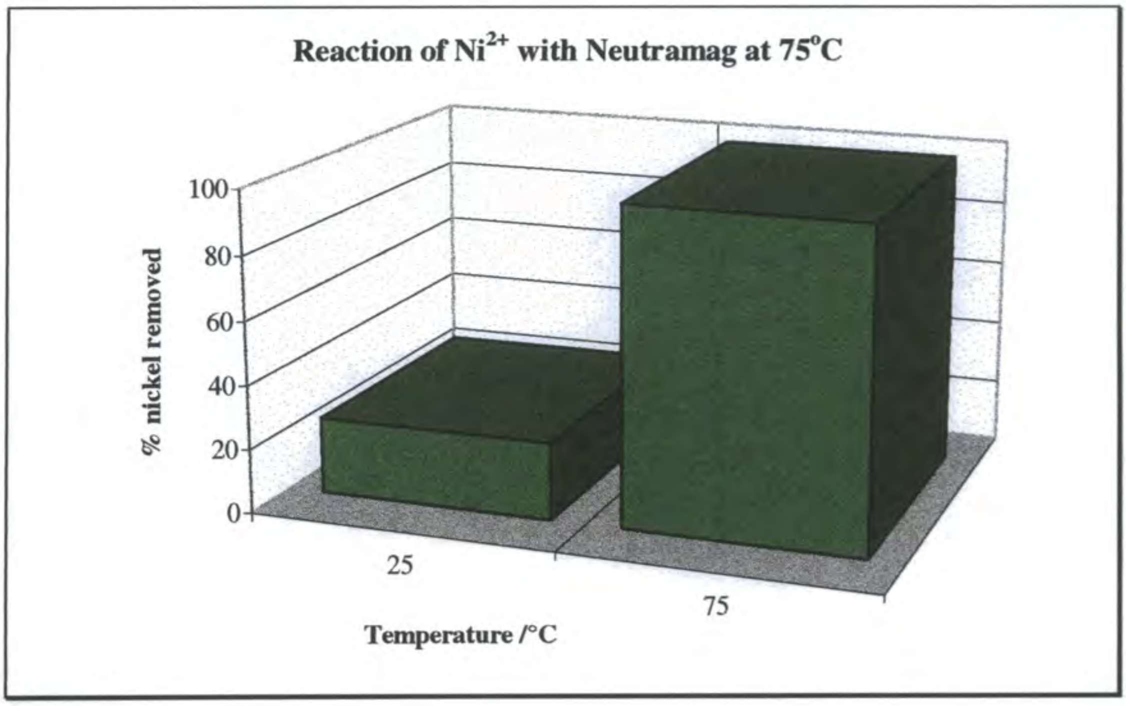

Figure 3.20

The heating appears to let the reaction continue after it would have normally stopped at room temperature, as well as increasing the rate at which the final amount of metal ion removal is achieved, **Figure 3.20**. This fits in well with the model proposed earlier, in **section 1.3**.

3.8.4.4 Summary.

Although good removals were achieved using high temperatures and donor ligands, this was not viable on an industrial scale. In general there was not the level of improvement in removal seen that was obtained in the previous M.Sc. project. This indicated that there were other factors affecting the reactions which could not be reproduced in the single metal systems.

3.8.5 Zinc.

Another difficult metal ion to treat was Zn^{2+}. It is commonly found in effluents from galvanizing works in concentrations of the order of 1000ppm. It was expected from the previous work that zinc would give similar results to Ni^{2+}. The use of various ligands was tested with Zn^{2+} to see if any improvements could be achieved.

3.8.5.1 Reactions with No Ligands.

The first reaction with a 10% excess of Neutramag on a 100ppm Zn^{2+} solution showed only a 15% removal, **section 3.5.2.1**, a poor level of removal like that achieved with Ni^{2+}. Increasing the concentration of the reactants tenfold gave a slight improvement with 20% being removed, **section 3.5.2.2**, and when left to react for four hours, **section 3.5.4**, nearly twice that metal ion removal was obtained, **Figure 3.21**.

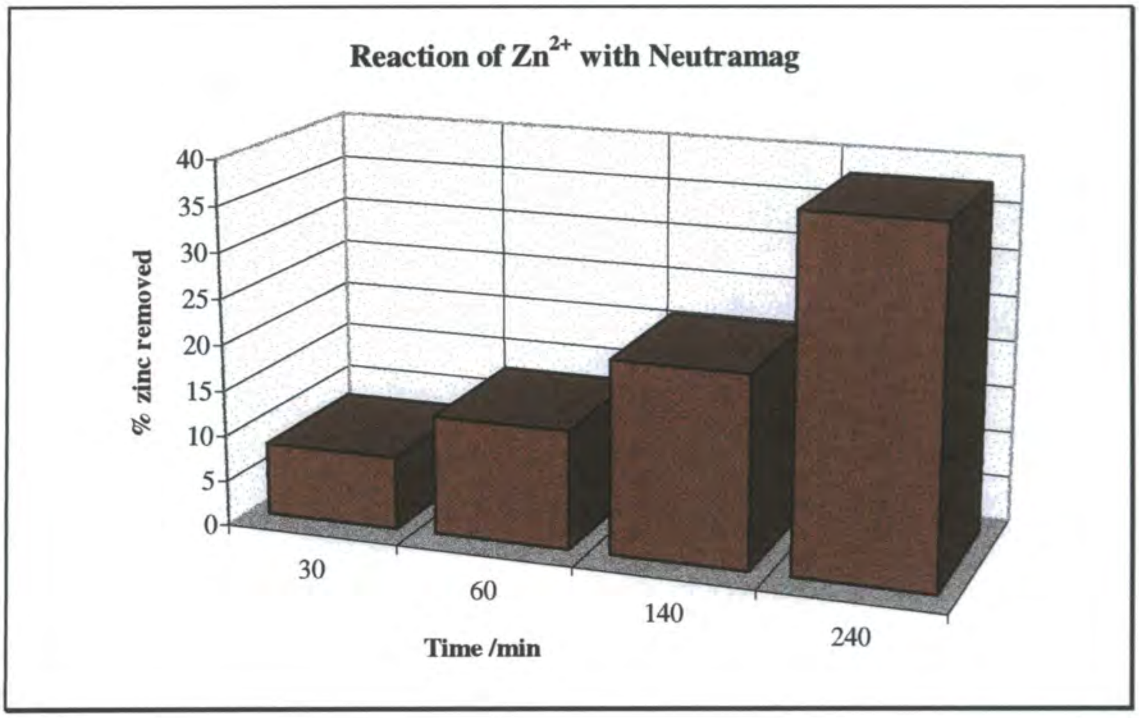

Figure 3.21

3.8.5.2 Reactions with Ligands.

Addition of PPh_3 showed that at a Zn^{2+}:PPh_3 ratio of 250:1 there was no difference in reaction over the period of an hour. Leaving a 100:1 ratio for just over 3 hours removed 30%. Exchanging the ligand for TMEDA showed improvement, more than 40% of the Zn^{2+} being removed from solution in four hours. Using bipy over four hours showed more improvement, removing approximately 50% from solution, **Figure 3.22**, although a reaction run for half the time removed much less, only 20%.

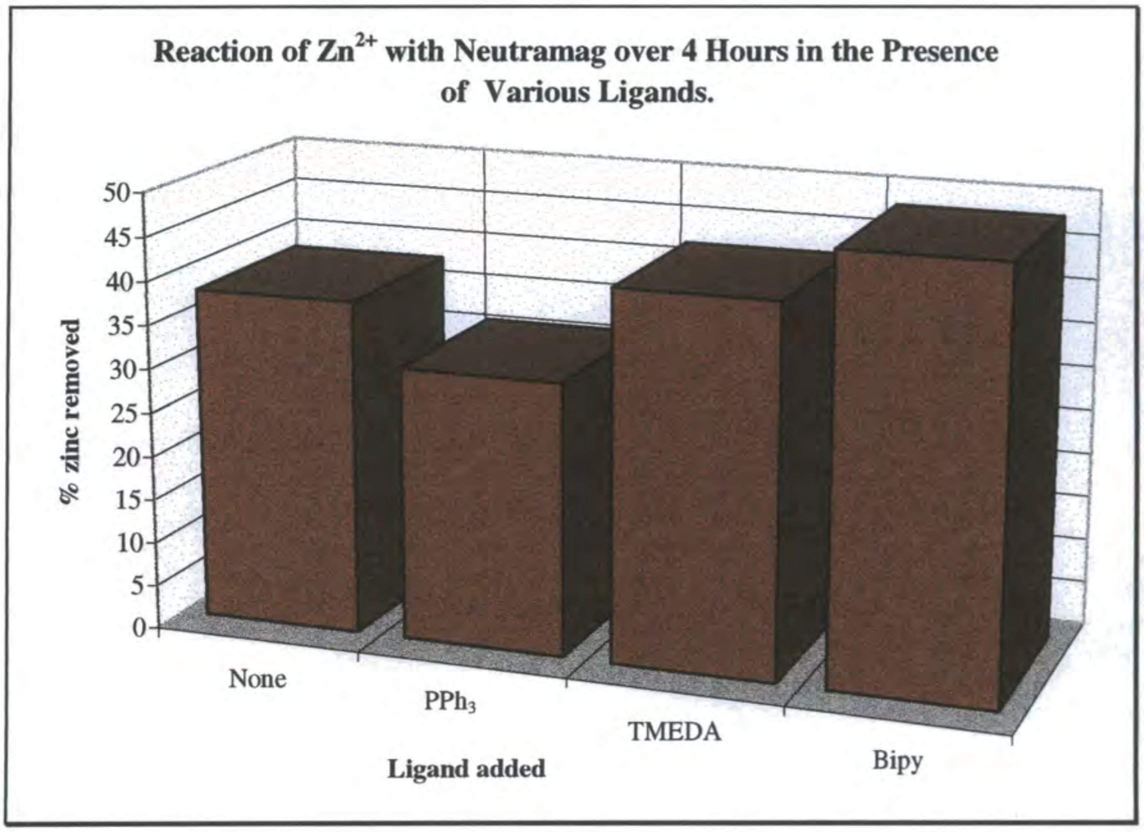

Figure 3.22

3.8.5.3 Summary

The benefits seen with the use of the N-donor ligands were not totally unexpected. Zn^{2+} is a hard metal centre, preferring to bond with the nitrogen rather than the sulphur in SCN^-, and so would interact much better with harder N-donors than with soft P-donors.

3.8.6 Lead.

Pb^{2+} salts are generally very insoluble [8], the only common salt that will dissolve in aqueous solution being the nitrate. Previous work had shown good removals and there was little problem expected with its treatment with Neutramag, **section 1.4**.

3.8.6.1 Reactions at 100ppm.

Reactions with 100ppm Pb^{2+} solutions using different ligands, PPh_3, TMEDA and bipy, at Pb^{2+}:L ratios of 100:1 over the course of 30 to 40 minutes were performed. These reactions showed very little change in the amount of lead precipitated, all giving ~55% Pb^{2+} removed, and it appeared that the ligands were having very little effect, **Figure 3.23**.

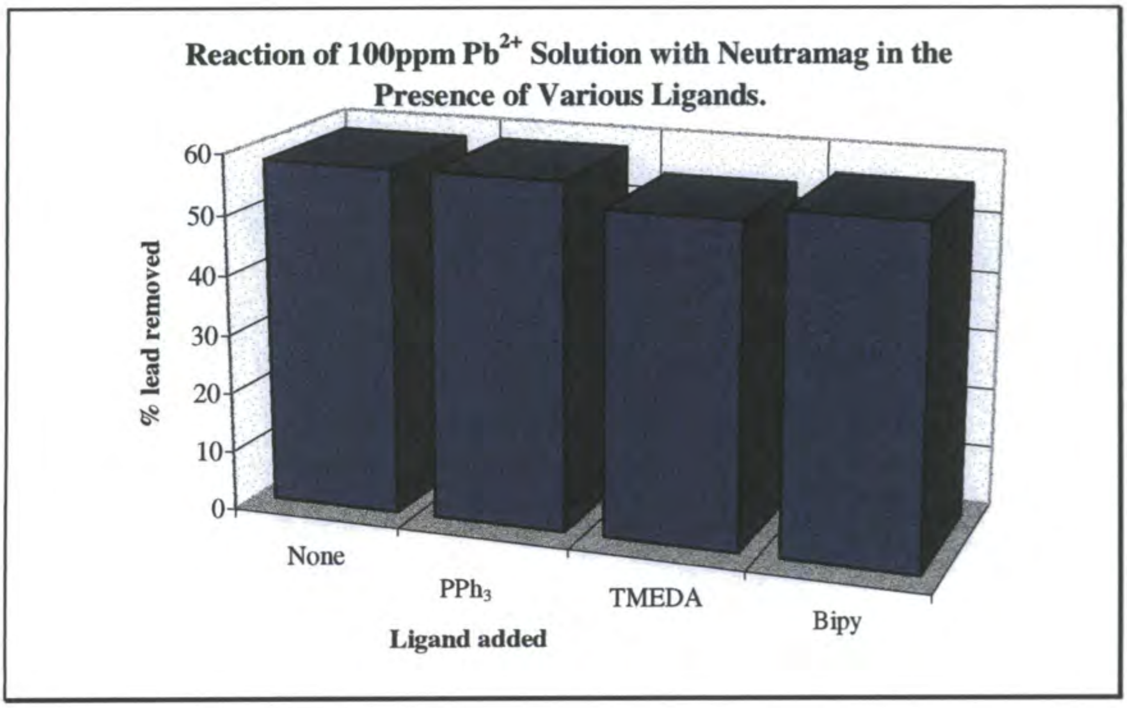

Figure 3.23

3.8.6.2 Reactions at 1000ppm.

Increasing the initial Pb^{2+} concentration to 1000ppm showed similar results. The reactions took approximately four times longer, but removed between 60 and 70% of the lead from solution. Each of the ligands was added at 100:1 Pb^{2+}:L ratios, **Figure 3.24**. To test if any extra reaction could be coaxed by the use of ligands, a reaction was performed using a 10:1 ratio of Pb^{2+}:TMEDA. This showed little change over the 100:1 reactions.

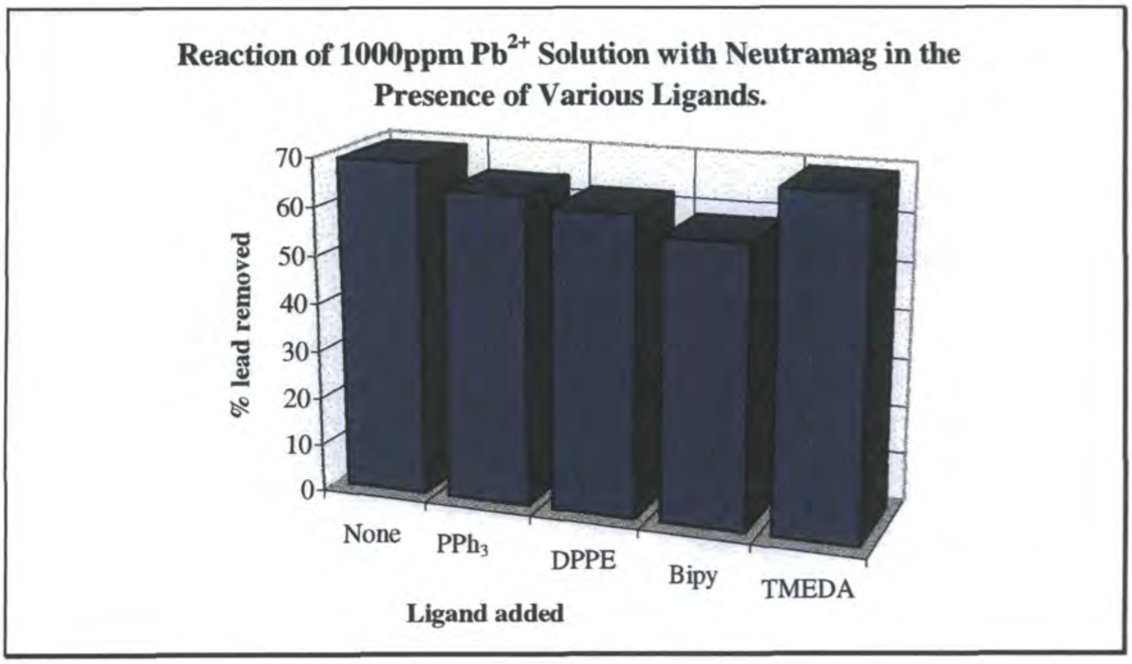

Figure 3.24

3.8.6.3 Summary.

The fact that the reactions gave better metal ion removals when left to react for a longer time would seem to indicate that they were incomplete when the pH levelled off. As the mixtures were left, after a certain length of time the pH started to decrease again. This is possibly due to the same reason as in the early part of the reaction with copper, abstraction of hydroxide ions from the water molecules.

Simply leaving the reactions to proceed for longer periods would seem to be the simplest solution to the treatment of this metal ion. Leaving effluents to react for too long is not viable on an industrial scale. The treatment with ligands did not affect the amounts of removal or the rates of reactions, and so treatment with these donor species was not a viable alternative.

3.8.7 Aluminium.

Al^{3+} was known to be a very easy metal ion to treat using Neutramag. Complete removal with very small excesses had been shown to be simple in previous work. It was thus very surprising when the first reaction failed to remove more than 15%, **section 3.7.1**. This was totally unexpected and went against all the previous work with Al^{3+}. Addition of a donor ligand, in this case PPh_3, was tried in an attempt to improve the metal ion removal, but only a 5% increase was observed.

Increasing the initial concentration of metal ions did not show any improvement, less than 10% of the aluminium being removed from solution in an hour. A different source of aluminium, from $Al_2(SO_4)_3$, produced a quite profoundly different result, **section 3.7.2.1**. All of the aluminium was removed from solution in less than half an hour with the treatment of the sulphate.

In order to check if the sulphate helped the reaction or the nitrate hindered it, reactions were undertaken with additional acid present, **section 3.7.2.2**. Treatment of both nitrate solution with sulphuric acid present and sulphate solution with nitric acid achieved 100% removals in under half an hour. The only reaction which had difficulty was the reaction of the nitrate only, **Figure 3.25**. This indicated that the presence of SO_4^{2-} aids the precipitation of aluminium in some way. It is possible that this is due to the formation of a more complicated precipitate than just the hydroxide. If the sulphate ions are precipitating in the reaction along with the hydroxide species such as $Al(OH)SO_4$ or $Al_2SO_4(OH)_4$ could be being formed. Without analysis of the precipitates this could not be accurately determined.

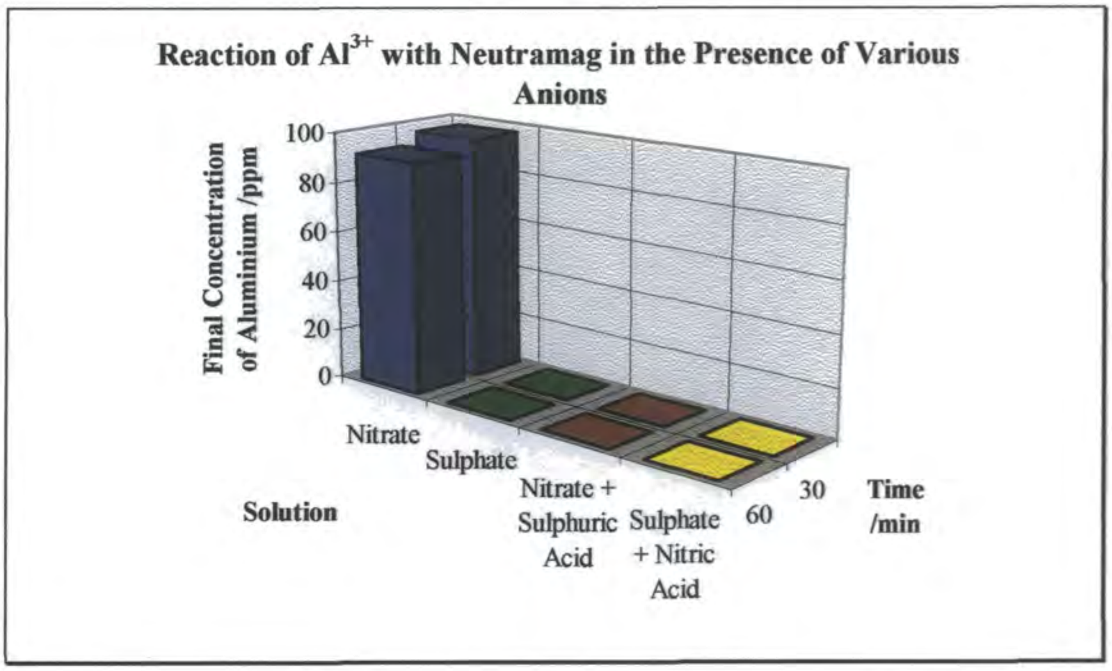

Figure 3.25

3.9 Conclusions.

The main thrust behind this section of the project was the identification of which donor ligands gave greatest improvements with which metal ions. The results seen in the previous project showed that the use of PPh_3 worked for most combinations. The work undertaken here on the single metal systems showed different results. For solutions of iron(II) there was the same increase in results seen with the addition of ligands, PPh_3 again emerging as the best additive. Other metal centres seemed greatly unresponsive to these additions, and no sizeable increases in metal ion removal were observed. This was strange as all ions were removed in greater quantities in the mixed systems studied in the previous projects. There must therefore, have been other reactions occurring in these mixed systems, which were not present in the single metal ion reactions. Treatment of copper(II) solutions with these ligands showed a noticeable decrease in metal ion removal, due to complex formation with the ligand.

It is possible that the ligands bind strongly enough with all the metal ions higher in the Irving-Williams series not to release the ligand again. This would only show up in the reactions where good metal ion removals were obtained without the ligand present, and the poor levels of removal of Ni^{2+} and Zn^{2+} would mask these results.

Aeration of iron(II) reactions has been shown to improve removal due to the ease with which iron (III) could be precipitated.

Aluminium precipitation has been shown to be much more difficult in the absence of sulphate ions.

Chapter 4

Studies on Mixed Metal Systems

4. Mixed Metal Systems.

4.1 Mixed Metal Reactions.

A solution was prepared by taking aliquots of prepared 10,000ppm metal ion solutions. 65.0ml of Fe^{2+} (1.16×10^{-2}mol), 18.0ml of Cu^{2+} (2.83×10^{-3}mol), 9.0ml of Zn^{2+} (1.38×10^{-3}mol), 4.0ml of Ni^{2+} (6.82×10^{-4}mol), 2.0ml of Pb^{2+} (9.65×10^{-5}mol) and 10.0ml of 0.998M HNO_3 (9.98×10^{-3}mol) were taken and diluted to a volume of 1000ml with deionised water. The pH of this solution was recorded. 8.1ml of PPh_3 solution was added, giving a M^{2+}:PPh_3 ratio of 266:1. The solution was aerated by bubbling compressed air through a perforated tube. 16.3ml of Neutramag slurry (2.32×10^{-2}mol) were added to the solution, giving a 10% excess over that needed for full stoichiometric reaction. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentrations of metals remaining in the filtrate determined by atomic absorption.

The reaction was repeated with one metal ion being omitted from the initial solution. Cu^{2+}, Zn^{2+}, and Pb^{2+} were omitted from separate reactions with 14.1ml (2.01×10^{-2}mol), 15.2ml (2.17×10^{-2}mol) and 16.2ml (2.31×10^{-2}mol) of Neutramag slurry, giving 10% excesses over that needed for full stoichiometric reaction. 5.2ml (5.2×10^{-5}mol), 5.7ml (5.7×10^{-5}mol), and 6.2ml (6.2×10^{-5}mol) of PPh_3 solution, giving M^{2+}:PPh_3 ratios of 266:1, were also added respectively.

The results are shown in **Table 4.1**.

Table 4.1

Metal Missing	**None**	**Copper**	**Zinc**	**Lead**
Volume of Neutramag added /ml	16.3	14.1	15.2	16.2
Initial pH	1.12	1.09	1.32	1.07
Time /min	40	120	100	30
Final pH	10.69	10.85	10.73	8.96
Final iron concentration /ppm	0.00	0.00	0.08	21
Final copper concentration /ppm	0.02	N/A	0.00	0.03
Final zinc concentration /ppm	0.01	0.01	N/A	0.59
Final nickel concentration /ppm	0.00	0.00	0.09	1.14
Final lead concentration /ppm	0.00	0.00	0.30	N/A

4.2 Two Metal Systems.

4.2.1 Nickel Reactions.

4.2.1.1 Reactions with $Fe^{(II)}$.

100ml of 10,000ppm Ni^{2+} solution (1.70×10^{-2}mol) and 100ml of 10,000ppm Fe^{2+} solution (1.79×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1000ppm, (1.70×10^{-2}M) and an initial Fe^{2+} concentration of 1000ppm, (1.79×10^{-2}M). The pH of this solution was recorded. 18.8ml of Neutramag slurry (3.97×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the iron species. A sample of the reaction mixture, approximately 80ml, was taken after 30 minutes and filtered to stop further reaction. The reaction was stopped after 60 minutes by filtration and the concentration of nickel and iron remaining in the filtrates determined by atomic absorption.

The reaction was repeated with the addition of 7.2ml of PPh_3 solution, 1.79×10^{-4}mol. This gave a Fe^{2+}:PPh_3 ratio of 100:1.

The results are shown in **Table 4.2**.

Table 4.2

Ligand	Time /min	pH	Nickel concentration /ppm	Iron concentration /ppm
None	0	2.96	1000	1000
	30	7.43	590	618
	60	7.24	525	510
PPh_3	0	2.15	1000	1000
	30	7.27	535	534
	60	7.29	410	435

4.2.1.2 Reactions with $Fe^{(III)}$.

100ml of 10,000ppm Ni^{2+} solution (1.70×10^{-2}mol) and 100ml of 10,000ppm Fe^{3+} solution (1.79×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1000ppm, (1.70×10^{-2}M) and an initial Fe^{3+} concentration of 1000ppm, (1.79×10^{-2}M). The pH of this solution was recorded. 21.6ml of Neutramag slurry (4.56×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the iron species. A sample of the reaction mixture, approximately 80ml, was taken after 30 minutes and filtered to stop further reaction. The reaction was stopped after 60 minutes by filtration and the concentration of nickel and iron remaining in the filtrates determined by atomic absorption.

The reaction was repeated with the addition of 7.2ml of PPh_3 solution, 1.79×10^{-4}mol. This gave a Fe^{3+}:PPh_3 ratio of 100:1.

The results are shown in **Table 4.3**.

Table 4.3

Ligand	**Time /min**	**pH**	**Nickel concentration /ppm**	**Iron concentration /ppm**
None	0	2.08	1000	1000
	30	8.01	326	0.10
	60	8.08	226	0.40
PPh_3	0	2.15	1000	1000
	30	8.12	333	0.65
	60	8.20	286	0.30

4.2.1.3 Reactions with Higher Excesses of Neutramag.

100ml of 10,000ppm Ni^{2+} solution (1.70×10^{-2}mol) and 100ml of 10,000ppm Fe^{3+} solution (1.79×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1000ppm, (1.70×10^{-2}M) and an initial Fe^{3+} concentration of 1000ppm, (1.79×10^{-2}M). The pH of this solution was recorded. 40.0ml of Neutramag slurry (4.92×10^{-2}mol) were added to the solution. giving a 30% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the iron species. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentrations of nickel and iron remaining in the filtrate determined by atomic absorption.

The reaction was repeated with a higher excess of Neutramag. 50.0ml of Neutramag slurry (6.15×10^{-2}mol) was added, giving an excess of 100% over that needed for full stoichiometric reaction with the nickel ions, but no excess for the iron species.

The results are shown in **Table 4.4**.

Table 4.4

% excess of Neutramag	Initial pH	Time /min	Final pH	Final nickel concentration /ppm	Final iron concentration /ppm
30	1.79	250	8.25	110	0.31
100	2.03	240	8.75	3.1	0.22

4.2.1.4 Reactions with 100ppm $Fe^{(III)}$.

100ml of 10,000ppm Ni^{2+} solution (1.70×10^{-2}mol) and 10ml of 10,000ppm Fe^{3+} solution (1.79×10^{-3}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1000ppm, (1.70×10^{-2}M) and an initial Fe^{3+} concentration of 100ppm, (1.79×10^{-3}M). The pH of this solution was recorded. 22.5ml of Neutramag slurry (2.76×10^{-2}mol) were added to the solution. giving a 45% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the iron species. The reaction was stopped after 60 minutes by filtration and the concentration of nickel and iron remaining in the filtrate determined by atomic absorption.

The reaction was repeated, allowing it to react until there was no further increase in pH.

The results are shown in **Table 4.5**.

Table 4.5

Initial pH	Time /min	Final pH	Final nickel concentration /ppm	Final iron concentration /ppm
2.65	60	9.05	760	0.10
2.80	150	7.72	750	0.04

4.2.1.5 Reaction at Lower Concentration.

10ml of 10,000ppm Ni^{2+} solution (1.70×10^{-3}mol) and 10ml of 10,000ppm Fe^{3+} solution (1.79×10^{-3}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 100ppm, (1.70×10^{-3}M) and an initial Fe^{3+} concentration of 100ppm, (1.79×10^{-3}M). The pH of this solution was recorded. 4.0ml of Neutramag slurry (5.48×10^{-3}mol) were added to the solution. giving a 64% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the iron species. The reaction was stopped after 60 minutes by filtration and the concentration of nickel and iron remaining in the filtrate determined by atomic absorption.

The results are shown in **Table 4.6**.

Table 4.6

Initial pH	Time /min	Final pH	Final nickel concentration /ppm	Final iron concentration /ppm
2.02	60	9.07	37	1.08

4.2.1.6 Reactions with $Al^{(III)}$.

100ml of 10,000ppm Ni^{2+} solution (1.70×10^{-2}mol) and 100ml of 10,000ppm Al^{3+} solution (3.70×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1000ppm, (1.70×10^{-2}M) and an initial Al^{3+} concentration of 1000ppm, (3.70×10^{-2}M). The pH of this solution was recorded. 35.2ml of Neutramag slurry (7.43×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the aluminium species. A sample of the reaction mixture, approximately 80ml, was taken after 30 minutes and filtered to stop further reaction. The reaction was stopped after 60 minutes by filtration and the concentration of nickel and aluminium remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.7**.

Table 4.7

Initial Al^{3+} concentration /ppm	Time /min	pH	Nickel concentration /ppm	Aluminium concentration /ppm
1000	0	2.61	1000	1000
	30	7.29	100	0.60
	60	7.93	18	0.50

The reaction was repeated using smaller amounts of aluminium. 100ppm (3.70×10^{-3}M) and 10ppm (3.70×10^{-4}M) solutions were used. 11.5ml (2.43×10^{-2}mol) and 9.2ml (1.93×10^{-2}mol) aliquots of Neutramag slurry were added to these solutions giving 10% excesses over that needed for full stoichiometric reaction with the nickel ions, but no excess for the aluminium species.

The results are shown in **Table 4.8**.

Table 4.8

Initial Al^{3+} concentration /ppm	Time /min	pH	Nickel concentration /ppm	Aluminium concentration /ppm
100	0	3.64	1000	100
	30	8.17	563	0.0
	60	8.53	468	0.0
10	0	4.47	1000	10
	30	8.38	970	0.0
	60	8.37	930	0.0

4.2.1.7 Reactions with $Cu^{(II)}$.

100ml of 10,400ppm Ni^{2+} solution (1.77×10^{-2}mol) and 100ml of 9,625ppm Cu^{2+} solution (1.51×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1040ppm, (1.77×10^{-2}M) and an initial Cu^{2+} concentration of 963ppm, (1.51×10^{-2}M). The pH of this solution was recorded. 12.9ml of Neutramag slurry (3.46×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the copper species. A sample of the reaction mixture, approximately 80ml, was taken after 30 minutes and filtered to stop further reaction. The reaction was stopped after 60 minutes by filtration and the concentration of nickel and copper remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.9**.

Table 4.9

Initial Cu^{2+} concentration /ppm	Time /min	pH	Nickel concentration /ppm	Copper concentration /ppm
1000	0	4.05	1040	963
	30	8.32	910	0.07
	60	8.35	905	0.05

The reaction was repeated using smaller amounts of copper. 100ppm (1.51×10^{-3}M) and 10ppm (1.51×10^{-4}M) solutions were used. 7.8ml (2.10×10^{-2}mol) and 7.3ml (1.96×10^{-2}mol) aliquots of Neutramag slurry were added to these solutions giving 10% excesses over that needed for full stoichiometric reaction with the nickel ions, but no excess for the copper species.

The results are shown in **Table 4.10**.

Table 4.10

Initial Cu^{2+} concentration /ppm	Time /min	pH	Nickel concentration /ppm	Copper concentration /ppm
100	0	3.96	1040	96.3
	30	8.25	925	0.10
	60	8.27	925	0.06
10	0	3.96	1040	9.6
	30	8.42	965	0.08
	60	8.43	960	0.01

4.2.2 Zinc Reactions.

4.2.2.1 Reaction with $Fe^{(III)}$.

4.2.2.1.1 Reaction at 10% Excess of Neutramag.

100ml of 10,000ppm Zn^{2+} solution (1.53×10^{-2}mol) and 100ml of 10,000ppm Fe^{3+} solution (1.79×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Zn^{2+} concentration of 1000ppm, (1.53×10^{-2}M) and an initial Fe^{3+} concentration of 1000ppm, (1.79×10^{-2}M). The pH of this solution was recorded. 20.7ml of Neutramag slurry (4.37×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the zinc ions, but no excess for the iron species. A sample of the reaction mixture, approximately 80ml, was taken after 30 minutes and filtered to stop further reaction. The reaction was stopped after 60 minutes by filtration and the concentration of zinc and iron remaining in the filtrates determined by atomic absorption.

The results are shown in **Table 4.11**.

Table 4.11

Time /min	pH	Zinc concentration /ppm	Iron concentration /ppm
0	1.84	1000	1000
30	7.51	220	0.01
60	7.66	160	0.02

4.2.2.1.2 Reactions at 37% Excess of Neutramag.

100ml of 10,000ppm Zn^{2+} solution (1.53×10^{-2}mol) and 100ml of 10,000ppm Fe^{3+} solution (1.79×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Zn^{2+} concentration of 1000ppm, (1.53×10^{-2}M) and an initial Fe^{3+} concentration of 1000ppm, (1.79×10^{-2}M). The pH of this solution was recorded. 35.0ml of Neutramag slurry (4.80×10^{-2}mol) were added to the solution, giving a 37% excess over that needed for full stoichiometric reaction with the zinc ions, but no excess for the iron species. The reaction was deemed to have finished when the pH stopped increasing. The solution was then filtered and the concentrations of zinc and iron remaining in the filtrate determined by atomic absorption.

The reaction was repeated using lower initial concentrations of metal ions. 10ml of each metal ion were added giving initial concentrations of 100ppm for each metal ion (1.53×10^{-3}M Zn^{2+}; 1.79×10^{-3}M Fe^{3+}) and treated with 3.5ml of Neutramag slurry (4.80×10^{-3}mol).

The results are shown in **Table 4.12**.

Table 4.12

Initial metal ion concentration /ppm	Initial pH	Time /min	Final pH	Final zinc concentration /ppm	Final iron concentration /ppm
1000	1.99	150	8.73	33	0.04
100	2.14	210	8.94	10	0.00

4.2.2.2 Reactions with $Al^{(III)}$.

100ml of 10,000ppm Zn^{2+} solution (1.53×10^{-2}mol) and 100ml of 10,000ppm Al^{3+} solution (3.70×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Zn^{2+} concentration of 1000ppm, (1.53×10^{-2}M) and an initial Al^{3+} concentration of 1000ppm, (3.7×10^{-2}M). The pH of this solution was recorded. 34.3ml of Neutramag slurry (7.24×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the zinc ions, but no excess for the iron species. A sample of the reaction mixture, approximately 80ml, was taken after 30 minutes and filtered to stop further reaction. The reaction was stopped after 60 minutes by filtration and the concentration of zinc and aluminium remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.13**.

Table 4.13

Initial Al^{3+} concentration /ppm	Time /min	pH	Zinc concentration /ppm	Aluminium concentration /ppm
1000	0	2.49	1000	1000
	30	7.48	12	0.8
	60	7.98	7.0	0.5

The reaction was repeated using smaller amounts of aluminium. 100ppm (3.70×10^{-3}M) and 10ppm (3.70×10^{-4}M) solutions were used. 11.5ml (2.24×10^{-2}mol) and 8.2ml (1.74×10^{-2}mol) aliquots of Neutramag slurry were added to these solutions giving 10% excesses over that needed for full stoichiometric reaction with the zinc ions, but no excess for the aluminium species.

The results are shown in **Table 4.14**.

Table 4.14

Initial Al^{3+} concentration /ppm	**Time /min**	**pH**	**Zinc concentration /ppm**	**Aluminium concentration /ppm**
100	0	3.21	1000	100
	30	6.92	310	0.0
	60	7.45	210	0.2
10	0	4.47	1000	10
	30	8.38	720	0.8
	60	8.37	700	0.5

4.2.2.3 Reactions with $Cu^{(II)}$.

4.2.2.3.1 Reactions at 10% Excess of Neutramag.

100ml of 9,750ppm Zn^{2+} solution (1.49×10^{-2}mol) and 100ml of 9,625ppm Cu^{2+} solution (1.51×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Zn^{2+} concentration of 975ppm, (1.49×10^{-2}M) and an initial Cu^{2+} concentration of 963ppm, (1.51×10^{-2}M). The pH of this solution was recorded. 11.8ml of Neutramag slurry (3.15×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the zinc ions, but no excess for the copper species. A sample of the reaction mixture, approximately 80ml, was taken after 30 minutes and filtered to stop further reaction. The reaction was stopped after 60 minutes by filtration and the concentration of zinc and copper remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.15**.

Table 4.15

Initial Cu^{2+} concentration /ppm	Time /min	pH	Zinc concentration /ppm	Copper concentration /ppm
1000	0	3.79	975	963
	30	7.33	198	0.28
	60	7.62	27	0.15

The reaction was repeated using smaller amounts of copper. 100ppm (1.51×10^{-3}M) and 10ppm (1.51×10^{-4}M) solutions were used. 6.7ml (1.79×10^{-2}mol) and 6.2ml (1.66×10^{-2}mol) aliquots of Neutramag slurry were added to these solutions giving 10% excesses over that needed for full stoichiometric reaction with the zinc ions, but no excess for the copper species.

The results are shown in **Table 4.16**.

Table 4.16

Initial Cu^{2+} concentration /ppm	Time /min	pH	Zinc concentration /ppm	Copper concentration /ppm
100	0	3.64	975	96.3
	30	7.31	738	0.42
	60	7.47	575	0.23
10	0	3.66	975	9.6
	30	7.25	880	1.33
	60	7.32	863	0.96

4.2.3 Iron(II) Reactions.

4.2.3.1 Reactions with Al$^{(III)}$.

100ml of 10,000ppm Fe^{2+} solution (1.79×10^{-2}mol) and 100ml of 10,000ppm Al^{3+} solution (3.70×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Fe^{2+} concentration of 1000ppm, (1.79×10^{-2}M) and an initial Al^{3+} concentration of 1000ppm, (3.70×10^{-2}M). The pH of this solution was recorded. 28.6ml of Neutramag slurry (7.53×10^{-2}mol) were added to the solution, giving a 10% excess over that needed for full stoichiometric reaction with the iron ions, but no excess for the aluminium species. A sample of the reaction mixture, approximately 80ml, was taken after 30 minutes and filtered to stop further reaction. The reaction was stopped after 60 minutes by filtration and the concentration of iron and aluminium remaining in the filtrates determined by atomic absorption.

The reactions was repeated with the addition of 7.2ml of PPh_3 solution (7.2×10^{-5}mol) which gave a Fe^{2+}:PPh_3 ratio of 250:1.

The results are shown in **Table 4.17**.

Table 4.17

Ligand added	Time /min	pH	Iron concentration /ppm	Aluminium concentration /ppm
None	0	2.56	1000	1000
	30	7.41	196	1.1
	60	7.82	10	0.5
PPh_3	0	2.58	1000	1000
	30	7.46	194	0.2
	60	7.66	30	0.5

4.3 Ferral Reactions.

The Ferral 2060 and Ferral Plus solutions, obtained from DuPont Chemicals, contained iron(III) and aluminium(III) salts. The concentrations of the metal ions were determined by atomic absorption. The concentration are shown in **Table 4.18**.

Table 4.18

Ferral Solution	Iron concentration /ppm	Aluminium concentration /ppm
Ferral 2060	16,840	36,000
Ferral Plus	14,000	37,000

4.3.1 Reactions of Nickel.

4.3.1.1 2.5ml of Ferral 2060.

100ml of 10,500ppm Ni^{2+} solution (1.79×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1050ppm, (1.79×10^{-2}M). 2.5ml of Ferral 2060 solution (7.55×10^{-4}M Fe^{3+}; 3.34×10^{-3}M Al^{3+}) were added to the solution. The pH of this solution was recorded. 10.1ml of Neutramag slurry (2.58×10^{-2}mol) were added to the solution, giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the $M^{(III)}$ species. Samples of the reaction mixture, approximately 80ml, were taken after 30, 60, 120 and 180 minutes and filtered to stop further reaction. The reaction was stopped after 240 minutes by filtration and the concentration of nickel, iron and aluminium remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.19**.

Table 4.19

Time /min	pH	Nickel concentration /ppm	Iron concentration /ppm	Aluminium concentration /ppm
0	3.06	1050	42	90
30	8.31	610	0.07	0.0
60	8.65	467	0.07	0.0
120	8.81	310	0.06	0.0
180	8.91	225	0.06	0.0
240	8.96	158	0.03	0.0

The reaction was repeated without the addition of the Ferral 2060 using the same amount of Neutramag, giving an excess of 44%. The results are shown in **Table 4.20**.

Table 4.20

Time /min	pH	Nickel concentration /ppm
0	3.98	1050
30	8.37	973
60	8.36	950
120	8.33	823
180	8.32	818
240	8.31	845

4.3.1.2 5.0ml of Ferral 2060.

100ml of 10,500ppm Ni^{2+} solution (1.79×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1050ppm, (1.79×10^{-2}M). 5.0ml of Ferral 2060 solution (1.51×10^{-3}M Fe^{3+}; 6.67×10^{-3}M Al^{3+}) were added to the solution. The pH of this solution was recorded. 11.6ml of Neutramag slurry (3.20×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the $M^{(III)}$ species. Samples of the reaction mixture, approximately 80ml, were taken after 30, 60, 120 and 180 minutes and filtered to stop further reaction. The reaction was stopped after 240 minutes by filtration and the concentration of nickel, iron and aluminium remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.21**.

Table 4.21

Time /min	pH	Nickel concentration /ppm	Iron concentration /ppm	Aluminium concentration /ppm
0	2.96	1050	84	180
30	7.26	455	0.04	0.0
60	7.71	270	0.04	0.0
120	7.82	53	0.04	0.0
180	8.61	2.0	0.04	0.0
240	8.86	1.3	0.09	0.0

The reaction was repeated without the addition of the Ferral 2060 using the same amount of Neutramag giving an excess of 79%. The results are shown in **Table 4.22**.

Table 4.22

Time /min	pH	Nickel concentration /ppm
0	3.98	1050
30	8.12	935
60	8.15	935
120	8.11	925
180	8.09	913
240	8.07	913

4.3.1.3 7.5ml of Ferral 2060.

100ml of 10,200ppm Ni^{2+} solution (1.74×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1020ppm, (1.79×10^{-2}M). 7.5ml of Ferral 2060 solution (2.27×10^{-3}M Fe^{3+}; 1.00×10^{-2}M Al^{3+}) were added to the solution. The pH of this solution was recorded. 14.0ml of Neutramag slurry (3.75×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the $M^{(III)}$ species. Samples of the reaction mixture, approximately 80ml, were taken after 30, 60, 120 and 180 minutes and filtered to stop further reaction. The reaction was stopped after 240 minutes by filtration and the concentration of nickel, iron and aluminium remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.23**.

Table 4.23

Time /min	pH	Nickel concentration /ppm	Iron concentration /ppm	Aluminium concentration /ppm
0	2.52	1020	84	180
30	7.35	363	0.05	0.0
60	7.57	130	0.06	0.0
120	8.68	3.4	0.06	0.0
180	8.86	2.2	0.07	0.0
240	8.84	1.2	0.07	0.0

The reaction was repeated without the addition of the Ferral 2060 using the same amount of Neutramag giving an excess of 116%. The results are shown in **Table 4.24**.

Table 4.24

Time /min	pH	Nickel concentration /ppm
0	3.92	1020
30	8.40	918
60	8.38	903
120	8.37	870
180	8.36	835
240	8.35	833

4.3.1.4 10.0ml of Ferral 2060.

100ml of 10,500ppm Ni^{2+} solution (1.79×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1050ppm, (1.79×10^{-2}M). 10.0ml of Ferral 2060 solution (3.02×10^{-3}M Fe^{3+}; 1.33×10^{-2}M Al^{3+}) were added to the solution. The pH of this solution was recorded. 17.4ml of Neutramag slurry (4.43×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the $M^{(III)}$ species. Samples of the reaction mixture, approximately 80ml, were taken after 30, 60, 120 and 180 minutes and filtered to stop further reaction. The reaction was stopped after 240 minutes by filtration and the concentration of nickel, iron and aluminium remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.25**.

Table 4.25

Time /min	pH	Nickel concentration /ppm	Iron concentration /ppm	Aluminium concentration /ppm
0	2.61	1050	168	360
30	7.29	355	0.02	0.0
60	7.53	295	0.05	0.0
120	8.38	3.7	0.05	0.0
180	8.47	3.5	0.06	0.0
240	8.41	1.8	0.09	0.0

The reaction was repeated without the addition of the Ferral 2060 using the same amount of Neutramag giving an excess of 148%. The results are shown in **Table 4.26**.

Table 4.26

Time /min	pH	Nickel concentration /ppm
0	3.98	1050
30	8.18	875
60	8.15	838
120	8.11	825
180	8.10	813
240	8.08	813

4.3.1.5 20.0ml of Ferral 2060.

100ml of 10,500ppm Ni^{2+} solution (1.79×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1050ppm, (1.79×10^{-2}M). 20.0ml of Ferral 2060 solution (6.04×10^{-3}M Fe^{3+}; 2.66×10^{-2}M Al^{3+}) were added to the solution. The pH of this solution was recorded. 27.0ml of Neutramag slurry (6.88×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the $M^{(III)}$ species. Samples of the reaction mixture, approximately 80ml, were taken after 30, 60, 120 and 180 minutes and filtered to stop further reaction. The reaction was stopped after 240 minutes by filtration and the concentration of nickel, iron and aluminium remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.27**.

Table 4.27

Time /min	pH	Nickel concentration /ppm	Iron concentration /ppm	Aluminium concentration /ppm
0	2.36	1050	84	180
30	7.15	194	0.10	0.0
60	7.66	28	0.10	0.0
120	8.06	3.6	0.11	0.0
180	8.13	2.1	0.12	0.0
240	8.11	1.6	0.13	0.0

The reaction was repeated without the addition of the Ferral 2060 using the same amount of Neutramag giving an excess of 285%. The results are shown in **Table 4.28**.

Table 4.28

Time /min	pH	Nickel concentration /ppm
0	3.99	1050
30	8.16	875
60	8.16	805
120	8.15	790
180	8.23	765
240	8.24	763

4.3.1.6 Reaction of Ferral Plus.

100ml of 10,000ppm Ni^{2+} solution (1.70×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1000ppm, (1.70×10^{-2}M). 10.0ml of Ferral Plus solution (2.51×10^{-3}M Fe^{3+}; 1.39×10^{-2}M Al^{3+}) were added to the solution. The pH of this solution was recorded. 17.0ml of Neutramag slurry (4.34×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the $M^{(III)}$ species. Samples of the reaction mixture, approximately 80ml, were taken after 30 and 60 minutes and filtered to stop further reaction. The reaction was stopped after 240 minutes by filtration and the concentration of nickel, iron and aluminium remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.29**.

Table 4.29

Time /min	pH	Nickel concentration /ppm	Iron concentration /ppm	Aluminium concentration /ppm
0	4.12	1000	140	376
30	7.29	325	0.04	0.1
60	7.36	213	0.03	0.0
240	8.36	2.0	0.02	0.0

4.3.2 Reactions of Zinc.

4.3.2.1 2.5ml of Ferral 2060.

100ml of 10,300ppm Zn^{2+} solution (1.58×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Zn^{2+} concentration of 1030ppm, (1.58×10^{-2}M). 2.5ml of Ferral 2060 solution (7.55×10^{-4}M Fe^{3+}; 3.34×10^{-3}M Al^{3+}) were added to the solution. The pH of this solution was recorded. 9.20ml of Neutramag slurry (2.35×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the $M^{(III)}$ species. Samples of the reaction mixture, approximately 80ml, were taken after 30, 60, 120 and 180 minutes and filtered to stop further reaction. The reaction was stopped after 240 minutes by filtration and the concentration of nickel, iron and aluminium remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.30**.

Table 4.30

Time /min	pH	Zinc concentration /ppm	Iron concentration /ppm	Aluminium concentration /ppm
0	3.01	1030	42	90
30	6.68	397	0.17	0.0
60	7.09	250	0.03	0.0
120	7.37	128	0.00	0.0
180	7.67	52	0.03	0.0
240	7.85	22	0.00	0.0

The reaction was repeated without the addition of the Ferral 2060 using the same amount of Neutramag giving an excess of 49%. The results are shown in **Table 4.31**.

Table 4.31

Time /min	pH	Zinc concentration /ppm
0	3.91	1050
30	7.21	893
60	7.21	873
120	7.18	850
180	7.21	800
240	7.23	715

4.3.2.2 5.0ml of Ferral 2060.

100ml of 10,300ppm Zn^{2+} solution (1.58×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Zn^{2+} concentration of 1030ppm, (1.58×10^{-2}M). 5.0ml of Ferral 2060 solution (1.51×10^{-3}M Fe^{3+}; 6.67×10^{-3}M Al^{3+}) were added to the solution. The pH of this solution was recorded. 11.61ml of Neutramag slurry (2.97×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the $M^{(III)}$ species. Samples of the reaction mixture, approximately 80ml, were taken after 30, 60, 120 and 180 minutes and filtered to stop further reaction. The reaction was stopped after 240 minutes by filtration and the concentration of nickel, iron and aluminium remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.32**.

Table 4.32

Time /min	pH	Zinc concentration /ppm	Iron concentration /ppm	Aluminium concentration /ppm
0	2.87	1030	84	180
30	6.59	321	0.33	0.0
60	6.72	135	0.04	0.0
120	7.58	4.3	0.01	0.0
180	8.37	0.6	0.05	0.0
240	8.39	0.6	0.03	0.0

The reaction was repeated without the addition of the Ferral 2060 using the same amount of Neutramag giving an excess of 88%. The results are shown in **Table 4.33**.

Table 4.33

Time /min	pH	Zinc concentration /ppm
0	3.91	1050
30	7.21	893
60	7.21	873
120	7.18	850
180	7.21	800
240	7.23	715

4.3.2.3 7.5ml of Ferral 2060.

100ml of 10,000ppm Zn^{2+} solution (1.53×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Zn^{2+} concentration of 1000ppm, (1.53×10^{-2}M). 7.5ml of Ferral 2060 solution (2.27×10^{-3}M Fe^{3+}; 1.00×10^{-2}M Al^{3+}) were added to the solution. The pH of this solution was recorded. 13.2ml of Neutramag slurry (3.53×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the $M^{(III)}$ species. Samples of the reaction mixture, approximately 80ml, were taken after 30, 60, 120 and 180 minutes and filtered to stop further reaction. The reaction was stopped after 240 minutes by filtration and the concentration of nickel, iron and aluminium remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.34**.

Table 4.34

Time /min	pH	Zinc concentration /ppm	Iron concentration /ppm	Aluminium concentration /ppm
0	2.55	1000	126	270
30	6.68	278	0.16	0.0
60	6.89	112	0.14	0.0
120	8.04	1.0	0.14	0.0
180	8.25	0.6	0.14	0.0
240	8.17	1.2	0.14	0.0

The reaction was repeated without the addition of the Ferral 2060 using the same amount of Neutramag giving an excess of 131%. The results are shown in **Table 4.35**.

Table 4.35

Time /min	pH	Zinc concentration /ppm
0	3.69	1000
30	7.57	888
60	7.57	850
120	7.59	828
180	7.59	780
240	7.60	703

4.3.2.4 10ml of Ferral 2060.

100ml of 10,300ppm Zn^{2+} solution (1.58×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Zn^{2+} concentration of 1030ppm, (1.58×10^{-2}M). 10.0ml of Ferral 2060 solution (3.02×10^{-3}M Fe^{3+}; 1.33×10^{-2}M Al^{3+}) were added to the solution. The pH of this solution was recorded. 17.4ml of Neutramag slurry (4.19×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the $M^{(III)}$ species. Samples of the reaction mixture, approximately 80ml, were taken after 30, 60, 120 and 180 minutes and filtered to stop further reaction. The reaction was stopped after 240 minutes by filtration and the concentration of nickel, iron and aluminium remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.36**.

Table 4.36

Time /min	pH	Zinc concentration /ppm	Iron concentration /ppm	Aluminium concentration /ppm
0	2.62	1030	168	360
30	6.72	189	0.50	0.0
60	7.07	19	0.03	0.0
120	7.81	0.5	0.03	0.0
180	7.75	0.7	0.04	0.0
240	7.71	1.7	0.06	0.0

The reaction was repeated without the addition of the Ferral 2060 using the same amount of Neutramag giving an excess of 166%. The results are shown in **Table 4.37**.

Table 4.37

Time /min	pH	Zinc concentration /ppm
0	3.88	1030
30	7.18	813
60	7.19	835
120	7.21	810
180	7.26	750
240	7.28	688

4.3.2.5 20ml of Ferral 2060.

100ml of 10,300ppm Zn^{2+} solution (1.58×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Zn^{2+} concentration of 1030ppm, (1.58×10^{-2}M). 20.0ml of Ferral 2060 solution (6.04×10^{-3}M Fe^{3+}; 2.66×10^{-2}M Al^{3+}) were added to the solution. The pH of this solution was recorded. 26.1ml of Neutramag slurry (6.65×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction with the nickel ions, but no excess for the $M^{(III)}$ species. Samples of the reaction mixture, approximately 80ml, were taken after 30, 60, 120 and 180 minutes and filtered to stop further reaction. The reaction was stopped after 240 minutes by filtration and the concentration of nickel, iron and aluminium remaining in the filtrates determined by atomic absorption. The results are shown in **Table 4.38**.

Table 4.38

Time /min	pH	Zinc concentration /ppm	Iron concentration /ppm	Aluminium concentration /ppm
0	2.45	1030	42	90
30	6.95	79	0.12	0.0
60	7.56	6.6	0.00	0.0
120	7.87	2.1	0.00	0.0
180	7.85	2.1	0.02	0.0
240	7.83	2.2	0.03	0.0

The reaction was repeated without the addition of the Ferral 2060 using the same amount of Neutramag giving an excess of 322%. The results are shown in **Table 4.39**.

Table 4.39

Time /min	pH	Zinc concentration /ppm
0	3.90	1030
30	7.20	750
60	7.24	718
120	7.33	618
180	7.37	565
240	7.38	493

4.4 Reactions with Differing Filtrations.

4.4.1 Reactions with Nickel.

100ml of 10,200ppm Ni^{2+} solution (1.74×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Ni^{2+} concentration of 1020ppm (1.74×10^{-2}M). The pH of this solution was recorded. 7.3ml of slurry (1.91×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction. The reaction was stopped after 60 minutes by filtration in two different ways. One sample was filtered as normal through a Whatman No. 1 filter paper and the other was filtered through a No. 3 porosity frit with ~1cm of celite. The concentration of nickel remaining in the filtrates was determined by atomic absorption.

The reaction was repeated with the addition of 5ml of Ferral 2060 solution (1.51×10^{-3}M Fe^{3+}; 6.67×10^{-3}M Al^{3+}) and 11.7ml of Neutramag slurry (3.14×10^{-2}mol). The reaction was filtered by the same two methods.

The results are shown in **Table 4.40**.

Table 4.40

Volume of Ferral 2060 added /ml	Initial pH	Final pH	Time /min	Final nickel concentration /ppm	
				Filter paper	Celite and frit
0.0	4.04	7.92	60	985	800
5.0	2.96	7.86	60	180	145

4.4.2 Reactions with Zinc.

100ml of 10,000ppm Zn^{2+} solution (1.53×10^{-2}mol) were taken and diluted to a volume of 1000ml with deionised water. This gave an initial Zn^{2+} concentration of 1000ppm (1.53×10^{-2}M). 5.0ml of Ferral 2060 solution (1.51×10^{-3}M Fe^{3+}; 6.67×10^{-3}M Al^{3+}) were added to the solution. The pH of this solution was recorded. 10.9ml of slurry (2.91×10^{-2}mol) were added to the solution. giving a 10% excess over that needed for full stoichiometric reaction. The reaction was stopped after 180 minutes by filtration in two different ways. One sample was filtered as normal through a Whatman No. 1 filter paper and the other was filtered through a No. 3 porosity frit with ~1cm of celite. The concentration of zinc remaining in the filtrates was determined by atomic absorption.

The reaction was repeated leaving it to react for 240 minutes.

The results are shown in **Table 4.41**.

Table 4.41

Initial pH	Final pH	Time /min	Final zinc concentration /ppm	
			Filter paper	Celite and frit
2.78	8.75	180	0.32	0.01
2.81	8.54	240	0.14	0.00

4.5 Discussion.

Studies on the single metal systems with addition of donor ligand species had not shown the same levels of improvements that had been seen in the previous project on actual effluent systems. Although Fe^{2+} did show beneficial results with the ligand, there were no significant improvements in the treatment of the other metal ions. This indicated that the effluents were affected by the presence of different metal ions in the solutions. In order to test this theory, solutions were studied which contained difficult to treat metal ions, i.e. Ni^{2+} and Zn^{2+}, along with other metal ions.

4.5.1 Mixed Metal Systems.

To confirm that the results seen in the previous studies were correct, solutions containing the same concentrations of metal ions as the synthetic effluents previously used were prepared. These contained a high concentration of Fe^{2+} (650ppm) with lower levels of Cu^{2+}(180ppm), Zn^{2+}(90ppm), Ni^{2+}(40ppm) and Pb^{2+}(20ppm). They also contained some nitric acid and PPh_3 in a 250:1 M^{2+}:PPh_3 ratio.

Treatment of this solution with Neutramag, at only a 10% excess, gave almost complete removal of all metal ions from solution, **section 4.1**. In order to see if any particular metal ion affected the removal of the others, the reaction was repeated with one of the ions being omitted from the initial solution. The only difference in any of these reactions was that the removal of the small amount of lead present at the start gave poorer removal for the other metal ions. The reaction was only left for 30 minutes and did not reach the pHs achieved in the other reactions. Leaving this reaction to continue for a longer time could well have improved the % metal ion removal down to the levels seen with the other reactions. The reactions with Cu^{2+} or Zn^{2+} missing took longer to go to completion, between two and three times the time with these metals present.

4.5.2 Two Metal Systems.

There was no clear trend seen through these three metal ion reactions and so a more considered approach was attempted. A usually difficult to treat metal ion, Ni^{2+} or Zn^{2+}, was mixed with other ions in standard amounts and their removal observed.

4.5.2.1 Nickel Reactions.

The first set of reactions looked at the treatment of Ni^{2+}. The first metal ion additive used was Fe^{2+}. This is not usually easy to treat with Neutramag to very low concentrations, although it was the main component in most of the effluent reactions where Ni^{2+} was successfully treated.

Starting with both metal ions present at 1000ppm, treatment with a 10% excess of Neutramag showed an increase in the amount of Ni^{2+} removed. Approximately 50% of each of the metal ions were removed from solution in an hour, **Figure 4.1**. The presence of the Fe^{2+} clearly affected the precipitation of the Ni^{2+}.

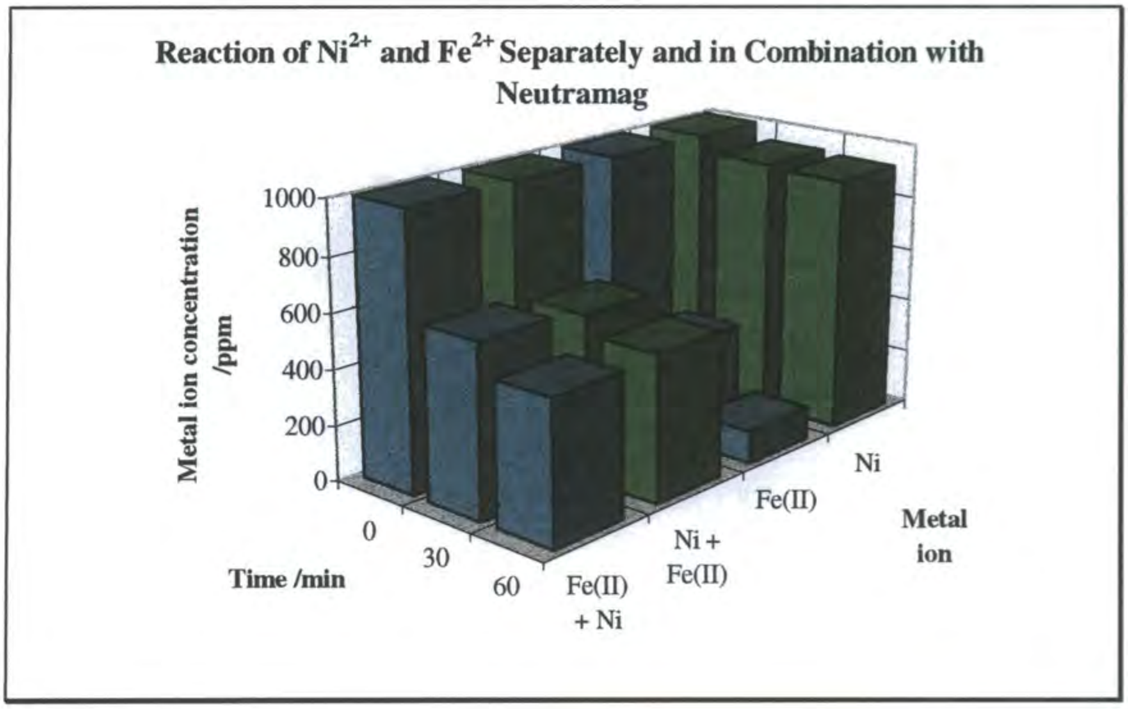

Figure 4.1

As Fe^{2+} reactions improved with the addition of donor ligand, the reaction was repeated with a 100:1 Fe^{2+}:PPh_3 ratio present. This showed further improvement to give a removal of about 60% of the Ni^{2+}, **Figure 4.2**.

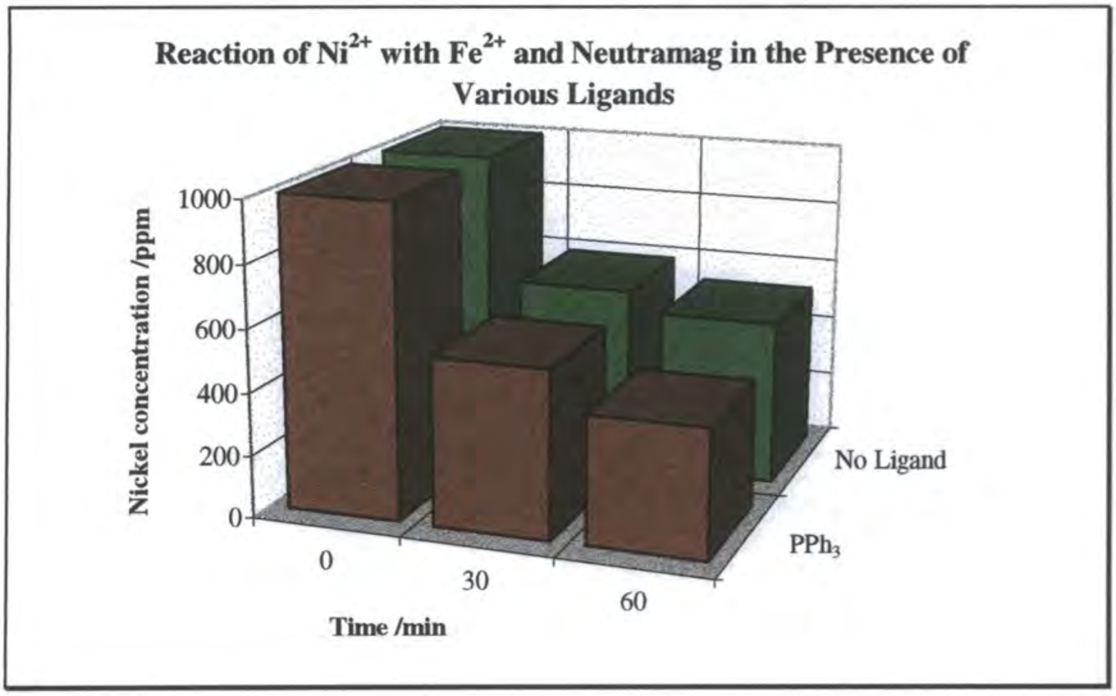

Figure 4.2

This was an improvement, but not to the levels seen previously. In the effluent reactions, the solutions were aerated to improve mixing and to oxidize Fe^{2+} to Fe^{3+}. With this in mind, the metal ion additive was changed to Fe^{3+}. Fe^{3+} is easily precipitated and so no excess was added for this ion, although a 10% excess was still added for the Ni^{2+} ions.

Greater improvement were seen for this reaction, a 75% of the Ni^{2+} being removed after an hour. These concentrations of Ni^{2+} have been previously unavailable from highly concentrated solutions without the use of heating. The Fe^{3+} has almost been completely removed from solution by the stage in the reaction when the Ni^{2+} starts to precipitate. This would seem to indicate that there is some sort of interaction with the solids

Treatment with PPh_3 present slightly decreased the removal in this case, **Figure 4.3**.

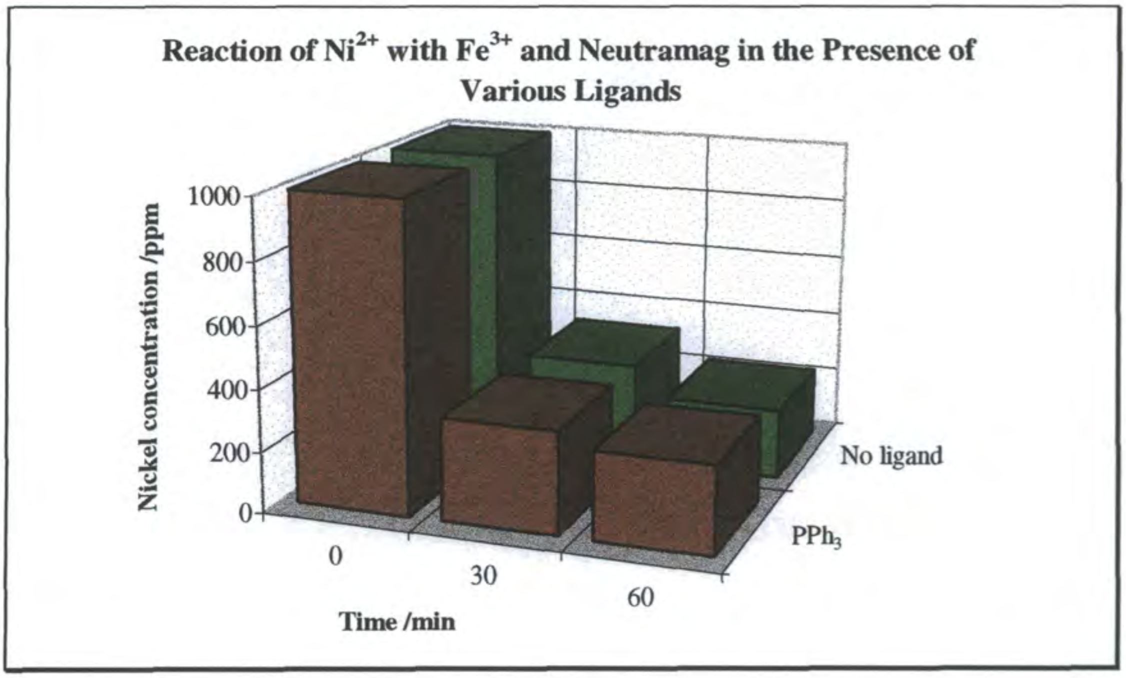

Figure 4.3

In an effort to increase the % metal ion removal further, reactions using higher excesses of Neutramag were attempted. Using 30% and 100% excesses gave very good metal ion removal; 90% was removed with 30% excess, but virtually all the Ni^{2+} was removed with twice the Neutramag after 4 hours, **Figure 4.4**.

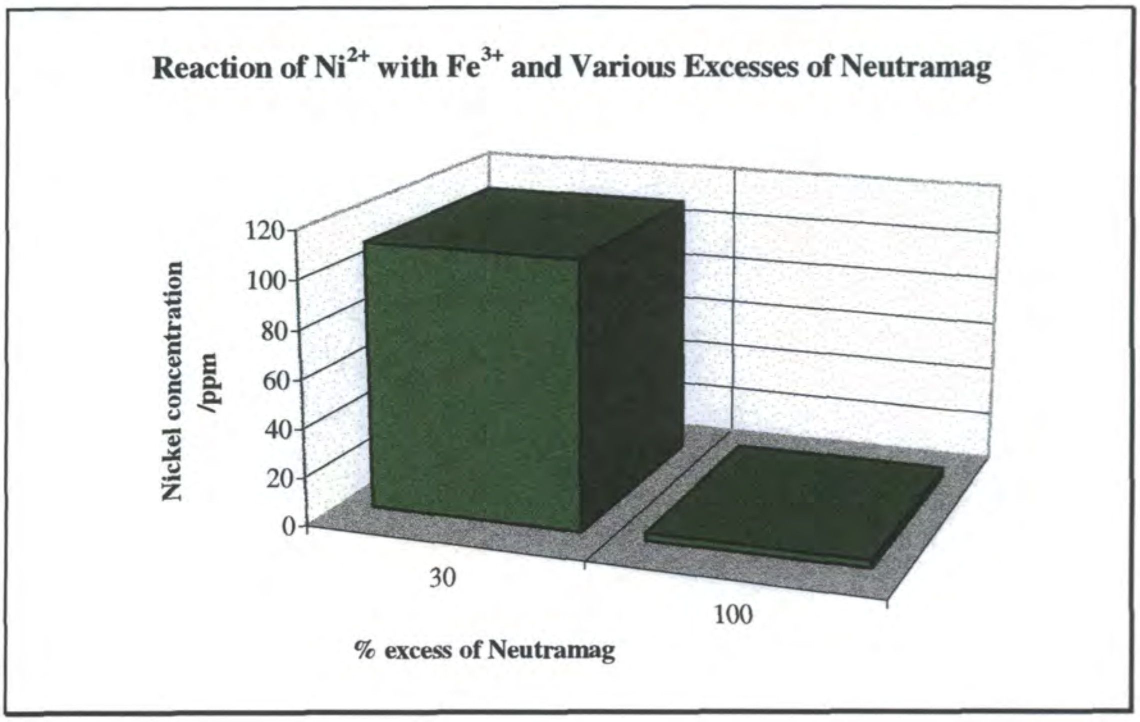

Figure 4.4

Reducing the concentration of Fe^{3+}in the initial solution, to 100ppm, with an excess of 45% Neutramag, showed little improvement over an hour, only 25% of Ni^{2+} being removed. Leaving the reaction to continue until the pH levelled off, a further 90 minutes, did not improve the removal. This showed a relationship between the improvement in metal ion removal with the amount of co-precipitating metal ion added. This was not a catalytic effect, as seen with Fe^{2+} and donor lignads, as the lesser addition of Fe^{3+} gave some improvement but cessation of the reaction still occurred. It also required significant quantities of Fe^{3+} to complete the reaction.

A reaction at lower concentrations of the initial solution, 100ppm for each metal ion, with 64% excess of Neutramag showed some improvement, with a 63% removal of Ni^{2+} being achieved. The relative increase in Fe^{3+} concentration again improved the amount of Ni^{2+} removed.

These results were very good in general, more Ni^{2+} being removed than previously seen with simple nickel reactions. To see if these improvements were due solely to the presence of Fe^{3+} or if another easily precipitated metal ion would show similar benefits to the reaction, Al^{3+} was tried in its place.

Starting with 1000ppm concentrations of both metal ions and a 10% excess of Neutramag for the Ni^{2+} ions only gave the best results yet seen. In just an hour, over 98% of Ni^{2+} ions had been removed from solution. Decreasing the levels of Al^{3+} in the initial solution decreased the % Ni^{2+} removed obtained, **Figure 4.5**. With 100ppm Al^{3+} ~50% of the Ni^{2+} was removed and with 10ppm Al^{3+} only 7% was removed.

Another easily precipitated metal ion, Cu^{2+}, was tested. The results were less encouraging. With an initial Cu^{2+} concentration of 963ppm only approximately 10% of the Ni^{2+} was removed and further lowering of the concentration decreased the removal to only 7% and 4% with 100 and 10ppm respectively, **Figure 4.6**. This divalent ion was less effective the the trivalent Fe^{3+} or Al^{3+}. It seemed reasonable that the higher charge on these species could be an influencing factor.

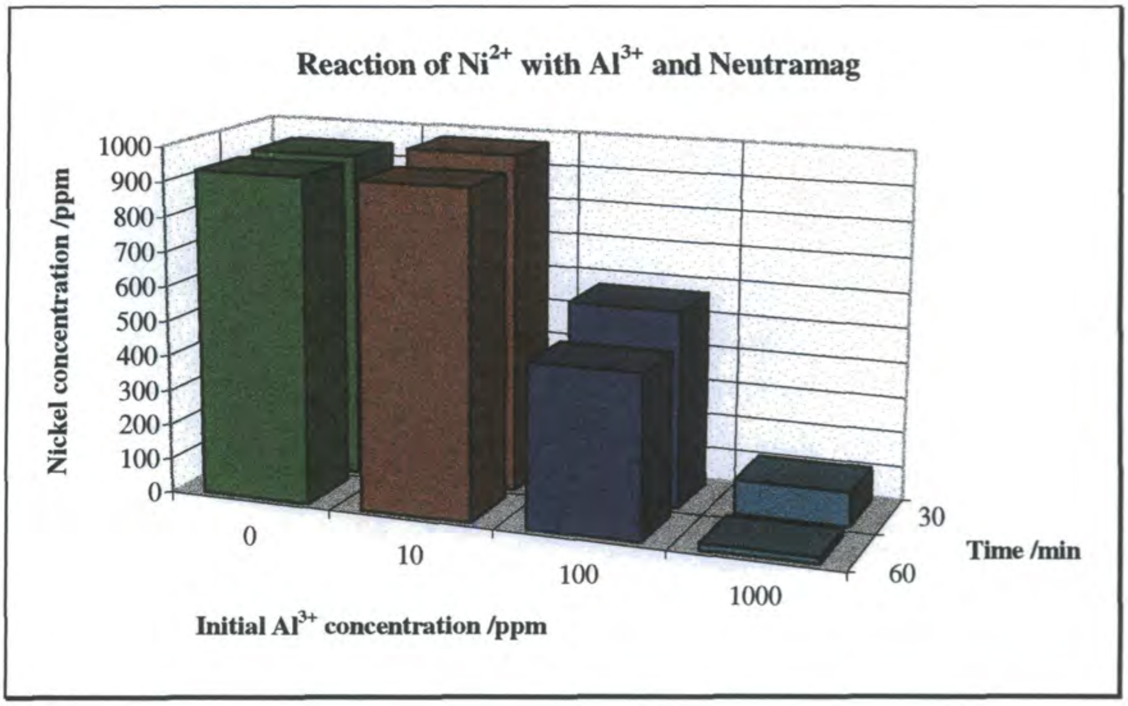

Figure 4.5

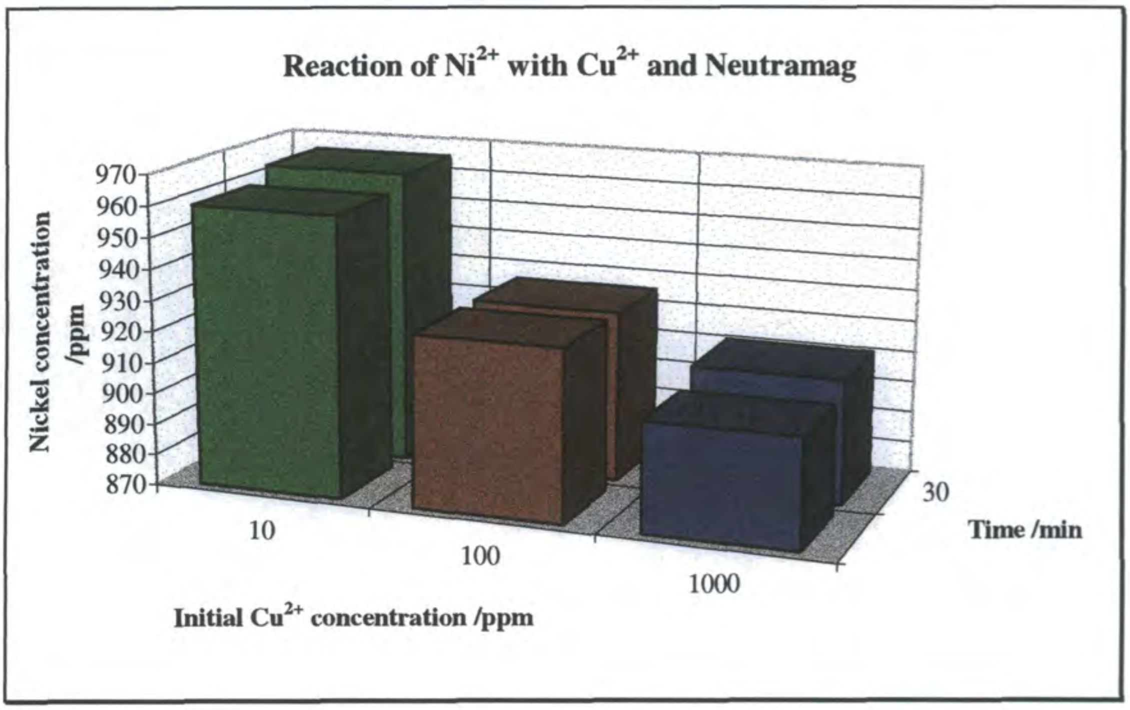

Figure 4.6

4.5.2.2 Reactions of Zinc.

Reactions were also performed using Zn^{2+} with the same metal ion additives present. Starting with 1000ppm of Fe^{3+} and a 10% excess of Neutramag, a metal ion removal of ~85% was achieved, **Figure 4.7**.

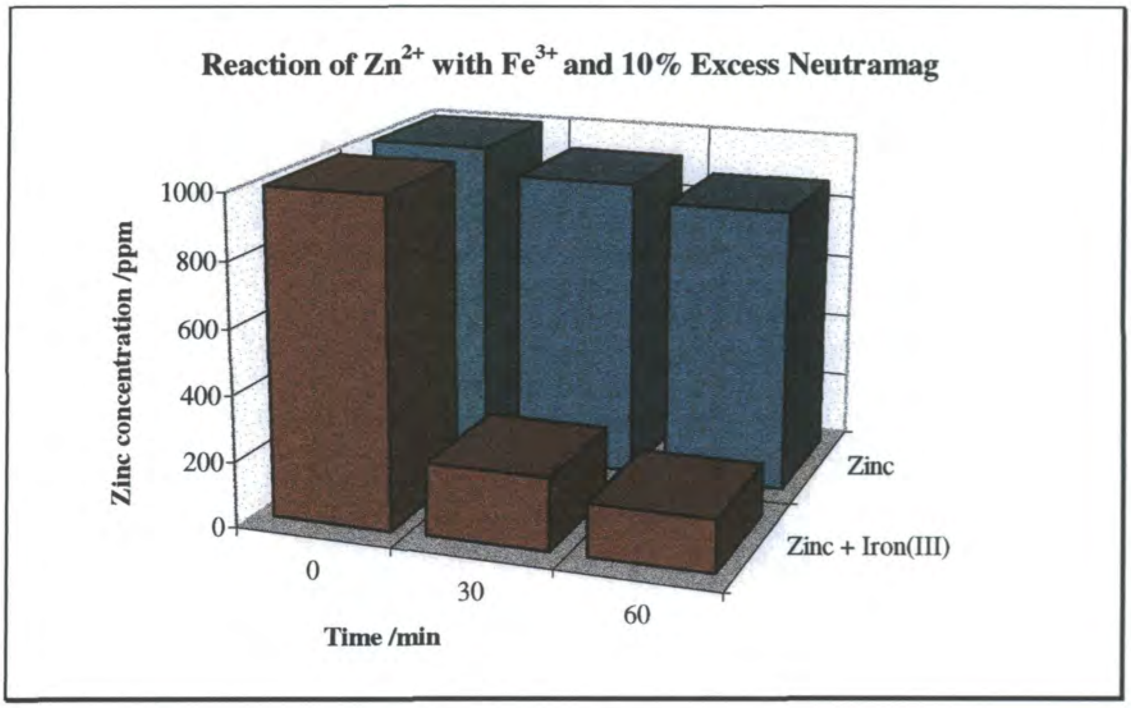

Figure 4.7

Increasing the excess of Neutramag to 37% further increased the metal ion removal to 97% although this took 2½ hours. Decreasing the initial concentrations of both metal ions to 100ppm gave a 90% removal after 3½ hours, **Figure 4.8**.

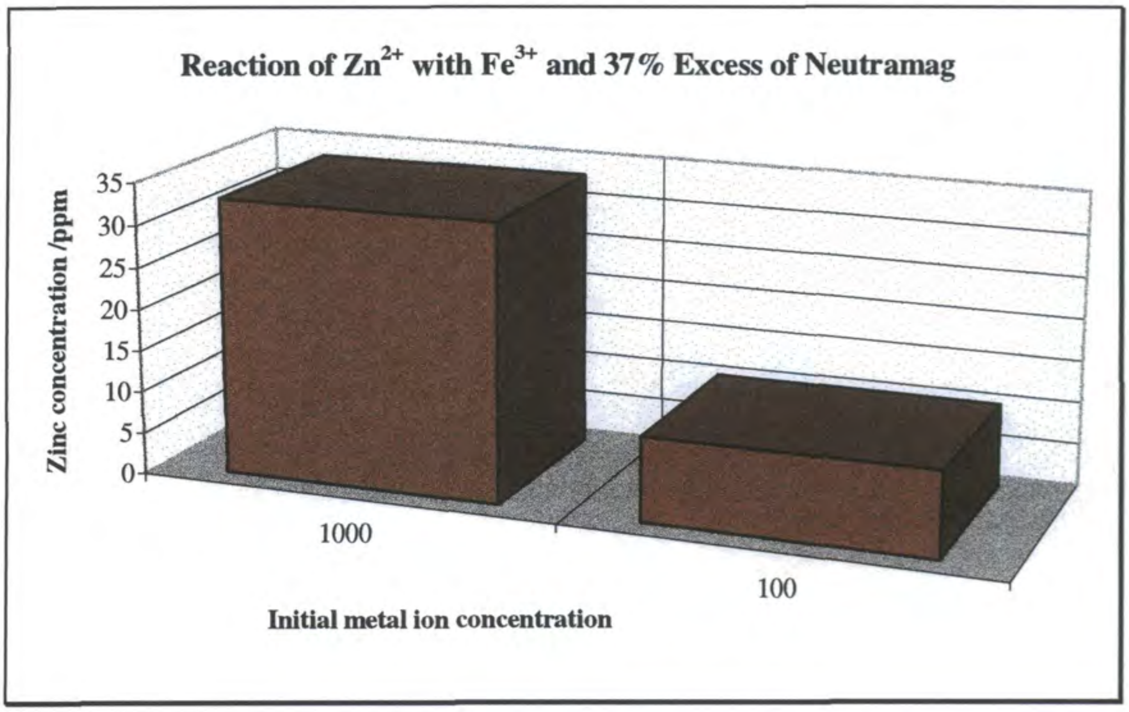

Figure 4.8

Replacing Fe^{3+} with Al^{3+} again improved the metal ion removal, >99% being obtained in an hour. This was very good for zinc treatment and almost achieved dischargable results. Decreasing the amount of Al^{3+} in the solution, decreased the metal ion removal to 80% for 100ppm and 30% for 10ppm, **Figure 4.9**.

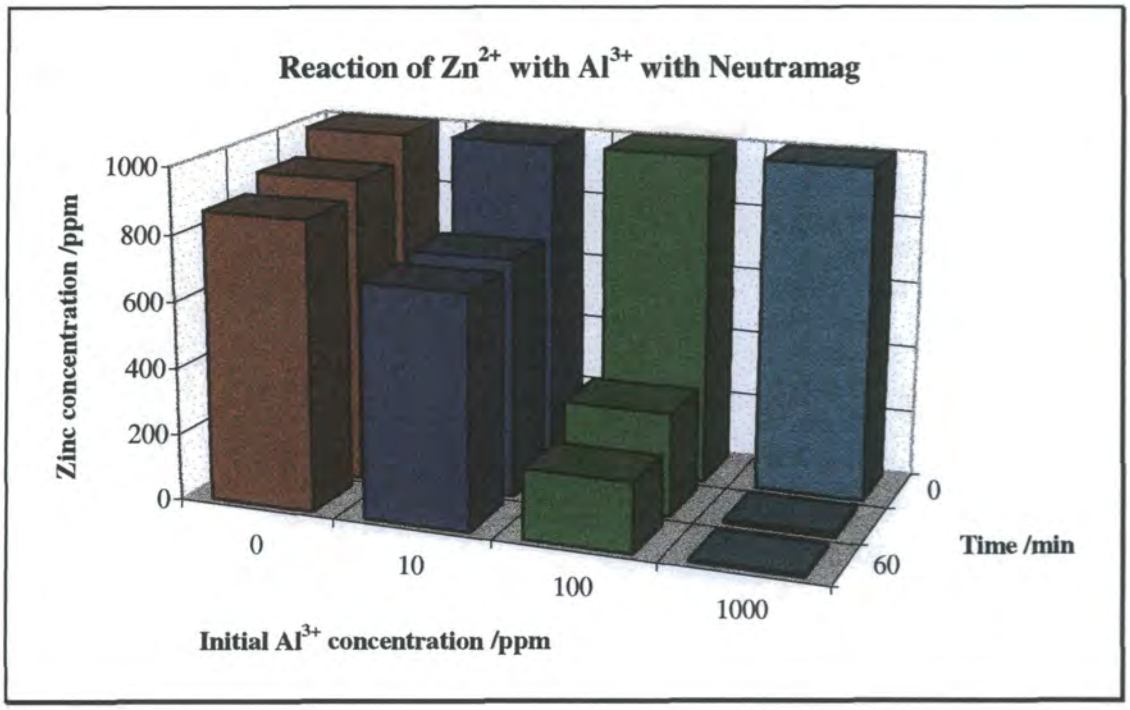

Figure 4.9

Addition of Cu^{2+} gave greater improvements in the precipitation of Zn^{2+} than it did with Ni^{2+}. 97% was removed with 1000ppm of Cu^{2+} and a 10 % excess of Neutramag. This figure decreased to 43% and 14% with 100ppm and 10ppm of Cu^{2+} respectively, **Figure 4.10**.

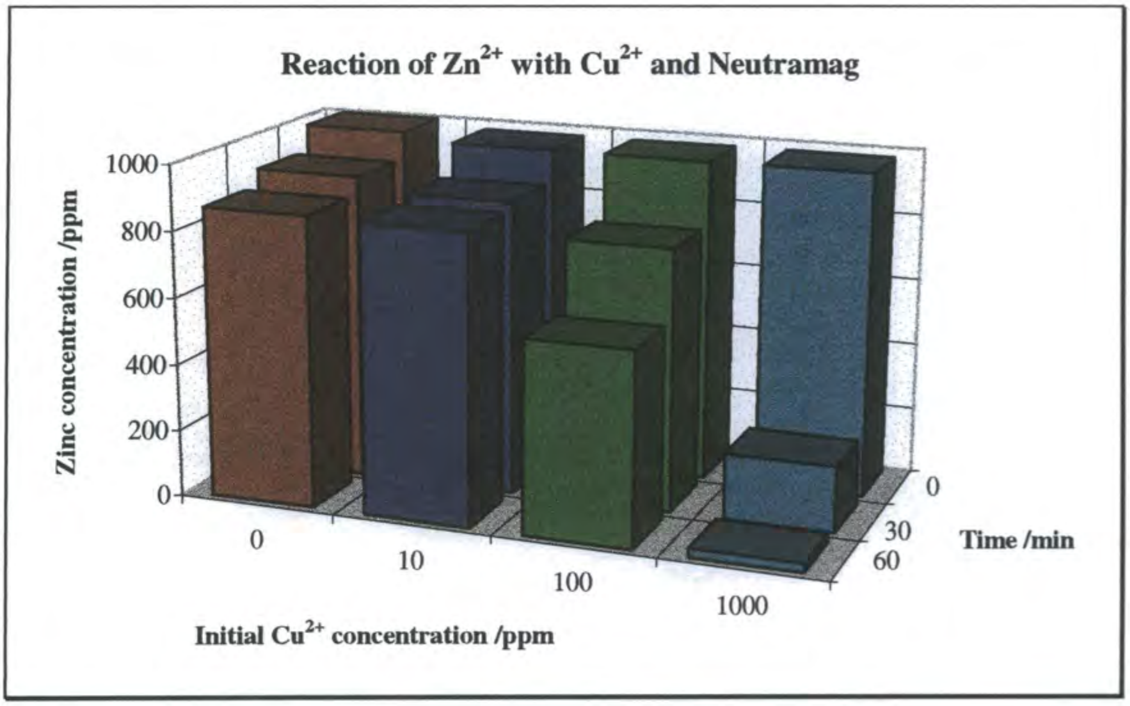

Figure 4.10

The trivalent metal ions again were superior in enhancing the reactions, but Cu^{2+} gave much better improvements with Zn^{2+} than with Ni^{2+}. This could again be due to the charge density on the interacting species, Zn^{2+} being smaller than Ni^{2+} due to contraction across the period.

4.5.2.3 Reactions of Iron$^{(II)}$.

Fe^{2+} was also tested in reactions with Al^{3+} present, which gave excellent results. The Fe^{2+} concentration dropped to well below levels usually seen in only 1 hour. Addition of PPh_3 to the reaction actually decreased the removal of Fe^{2+} although it was still much higher than normally achieved with PPh_3 in the time, **Figure 4.11**.

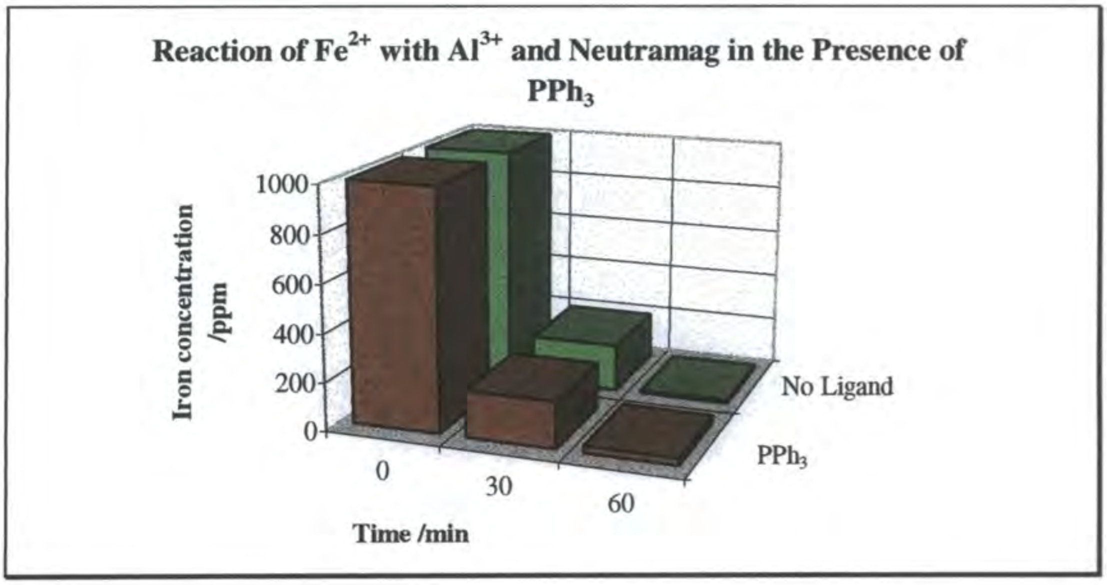

Figure 4.11

4.5.3 Reactions with Ferral.

During the previous reactions with M^{3+} additives, a commercially available product was found and brought in to test in a similar fashion. The solution consisted of mainly Fe^{3+} and Al^{3+} sulphates with some acid present. The concentrations of Fe^{3+} and Al^{3+} were determined by atomic absorption, **Table 4.18**,and the values used to calculate how much more Neutramag was needed for the precipitation of the M(III) species, **section 4.3**. This did not take into account any other acidic species which were present and so the excess of Neutramag used was actually lower than that quoted, which makes the results all the more impressive. There were two grades of Ferral, Ferral 2060 and Ferral Plus. The Ferral Plus contained an additional component, a polymer which aided the precipitation of metal ions. Most of the reactions looked at the effect of the more simple M$^{(III)}$ solutions of Ferral 2060.

4.5.3.1 Reactions of Nickel

The reactions were performed using increasing quantities of Ferral 2060; 2.5, 5. 7.5, 10 and 20ml aliquots were added. In each of these reactions samples were taken at regular intervals so the course of the reaction could be followed with concentrations being obtained, rather than just by following the pH.

With each addition of Ferral 2060, increased amounts of Neutramag were required in order to treat the solutions. In each case a control reaction was performed which used the same amount of Neutramag as in the Ferral reaction, but with no Ferral being present. This gave much larger excesses and showed that the benefits seen were due to more than just the increased levels of Neutramag present.

Figure 4.12 - **Figure 4.16** show the concentrations of nickel achieved using Ferral 2060 and with the same amounts of Neutramag. They clearly show the improvements seen with the addition of the Ferral solution.

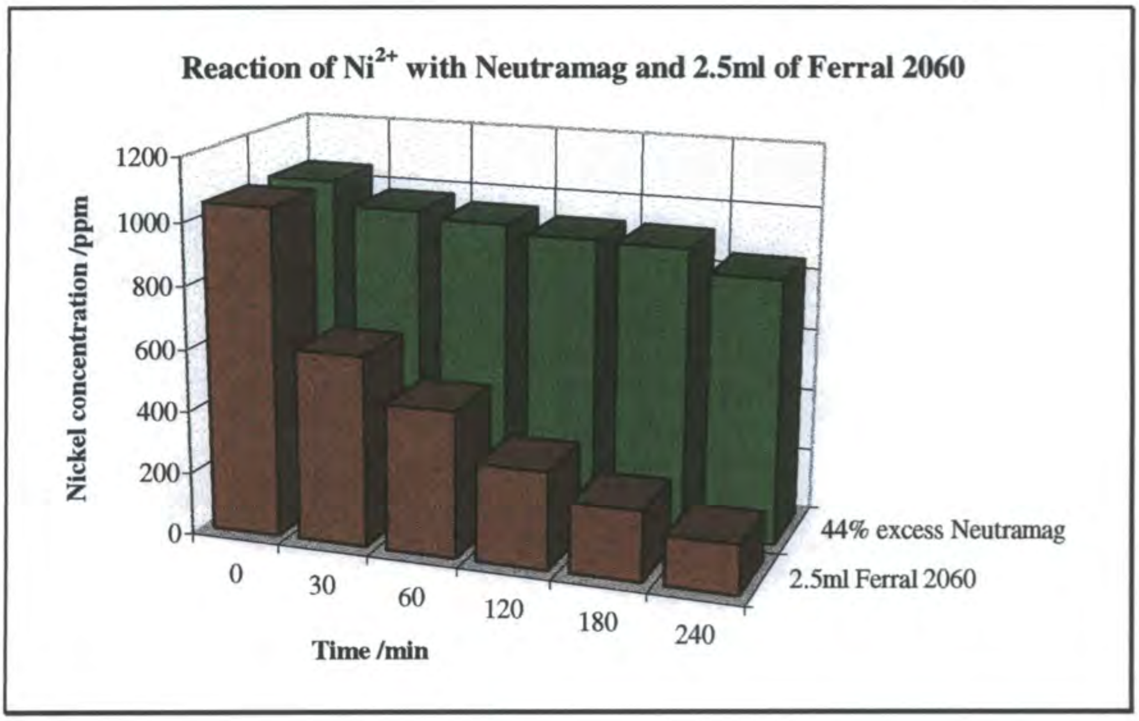

Figure 4.12

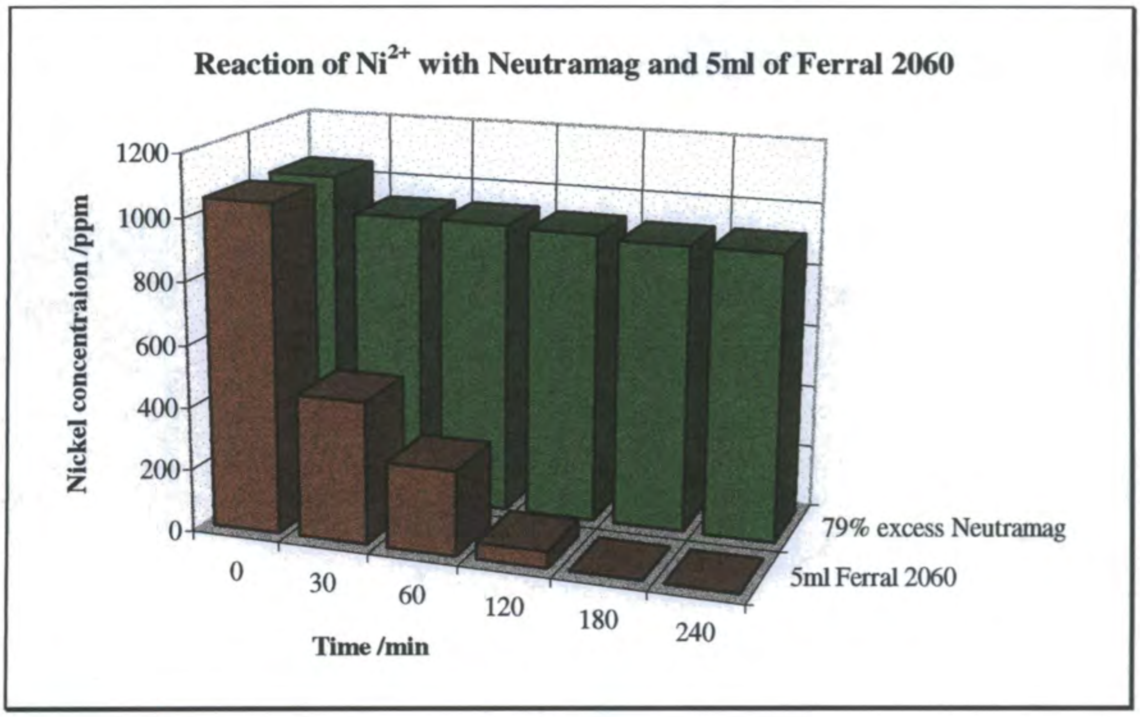

Figure 4.13

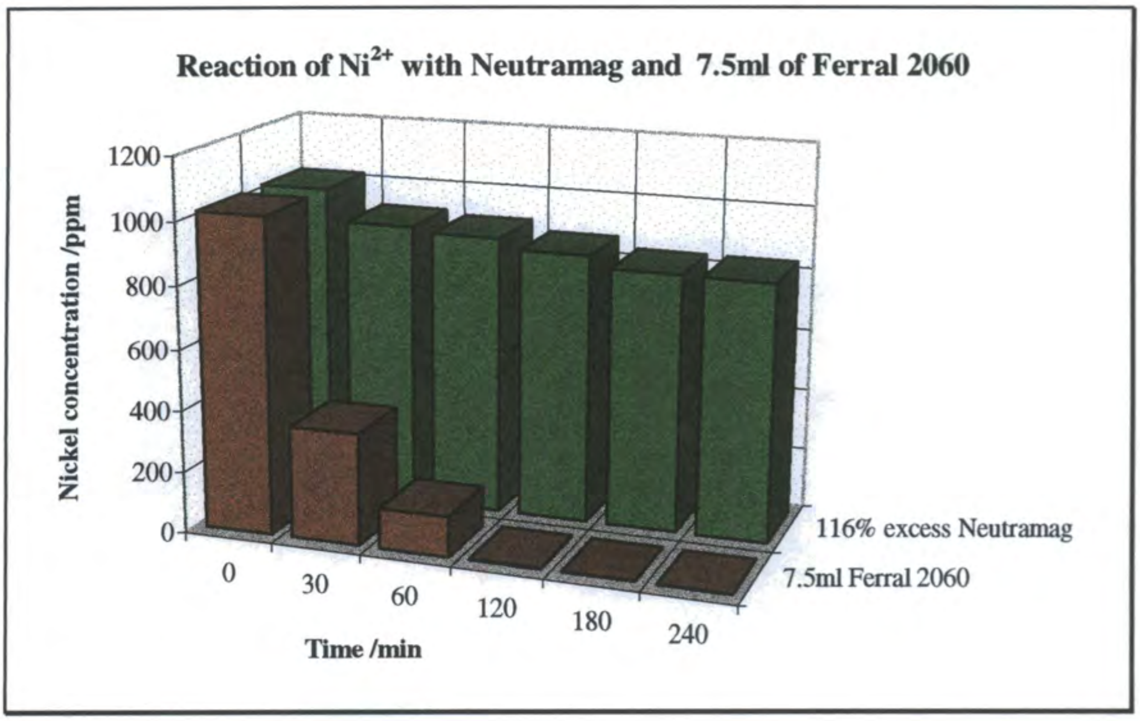

Figure 4.14

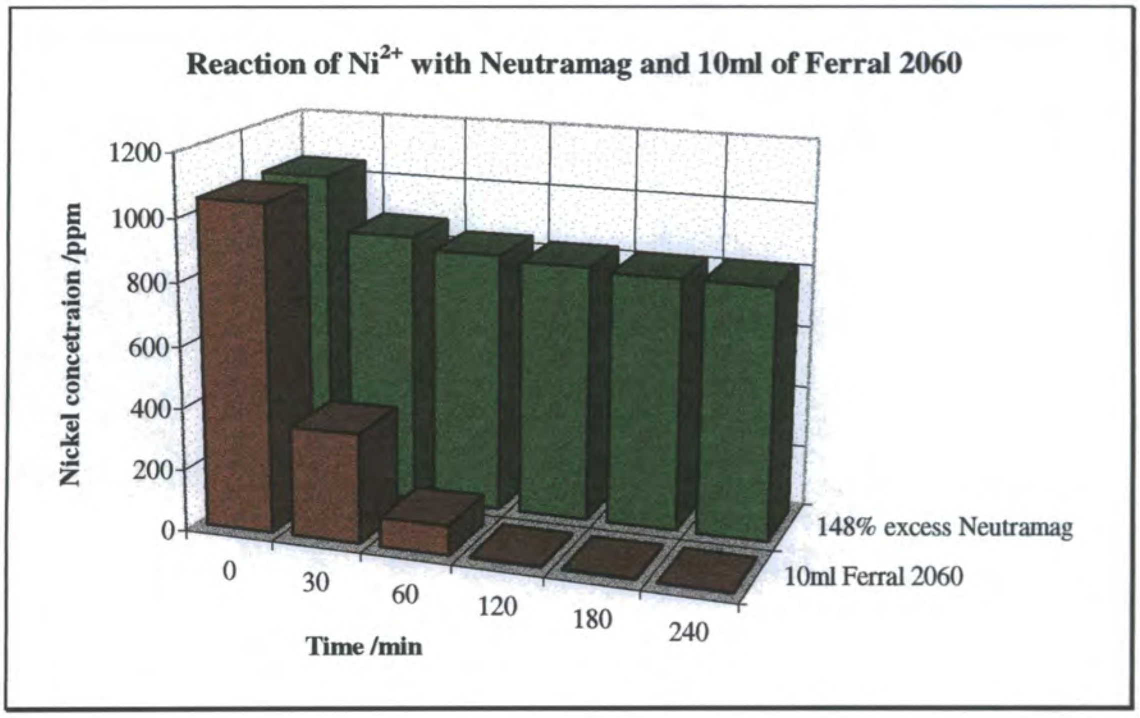

Figure 4.15

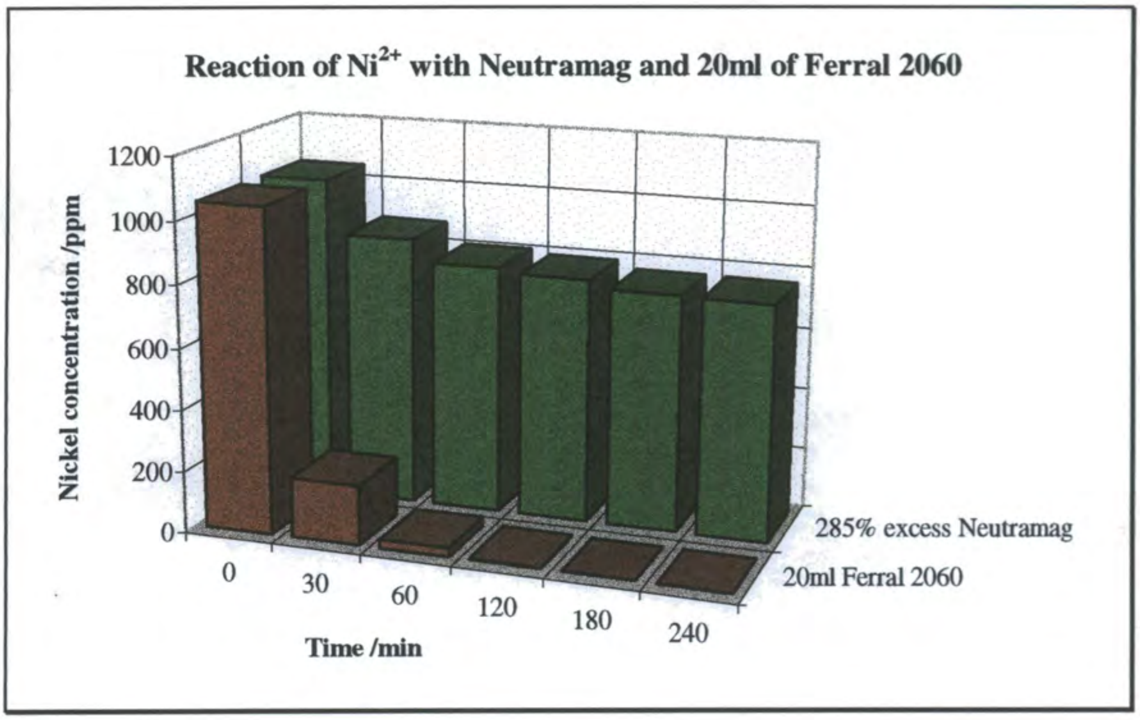

Figure 4.16

Figure 4.17 shows relative percentages removed by the various aliquots of Ferral 2060 added. It is clearly seen that increasing the amount of Ferral 2060 added increases the amount removed and the rate at which the higher removal is achieved.

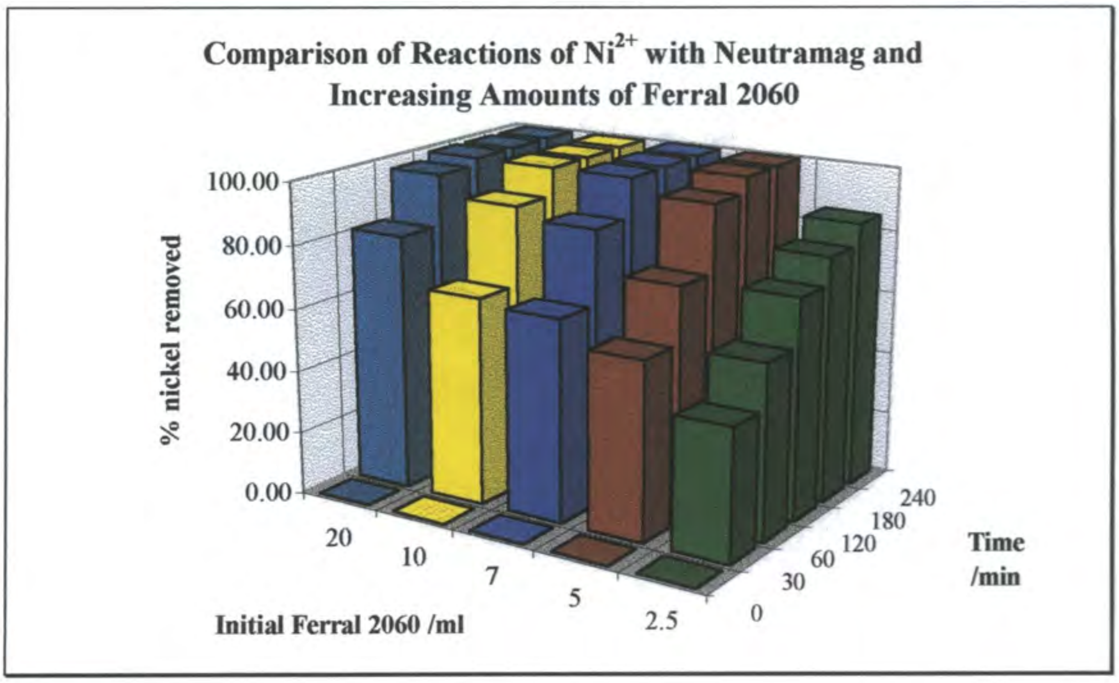

Figure 4.17

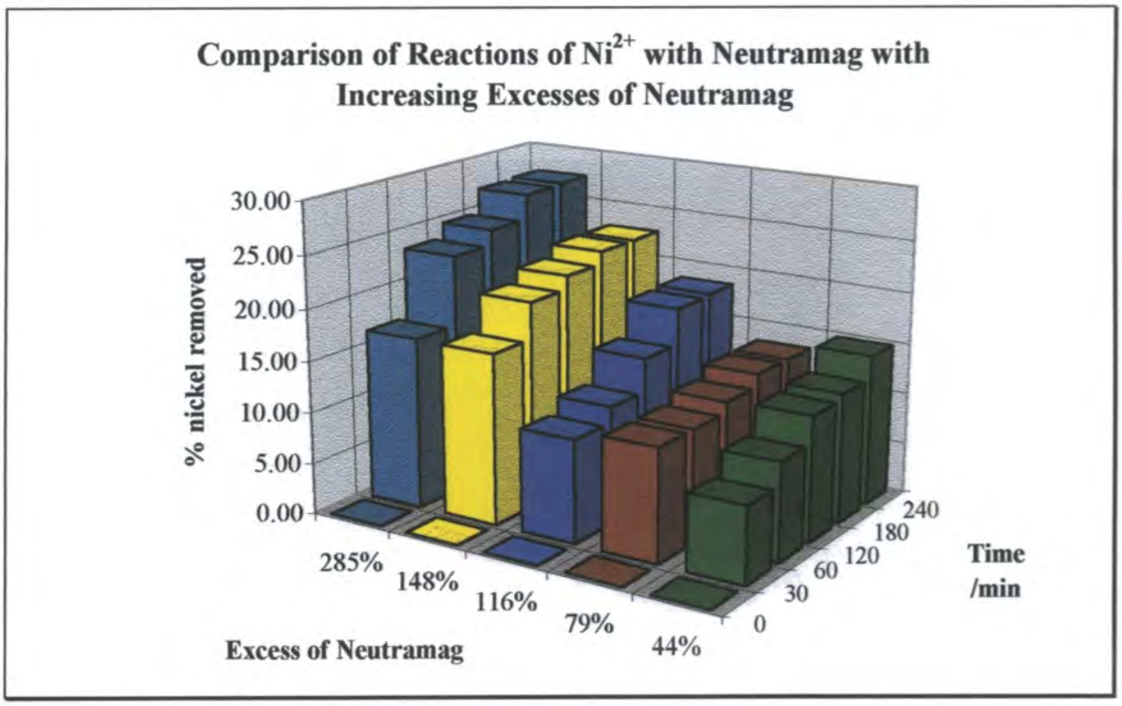

Figure 4.18

Figure 4.18 shows the variation in percentage nickel removed with the higher excesses of Neutramag.

Figure 4.19 shows the % improvement, the difference in % Ni^{2+} removed, with the addition of the Ferral 2060 over the simple excess of Neutramag for each amount of Ferral added. It can be seen that the greatest improvement was found with the addition of 5ml of Ferral 2060 after 3 hours. Although the higher additions of Ferral gave lower final concentrations, better results were also obtained with straight addition of extra Neutramag.

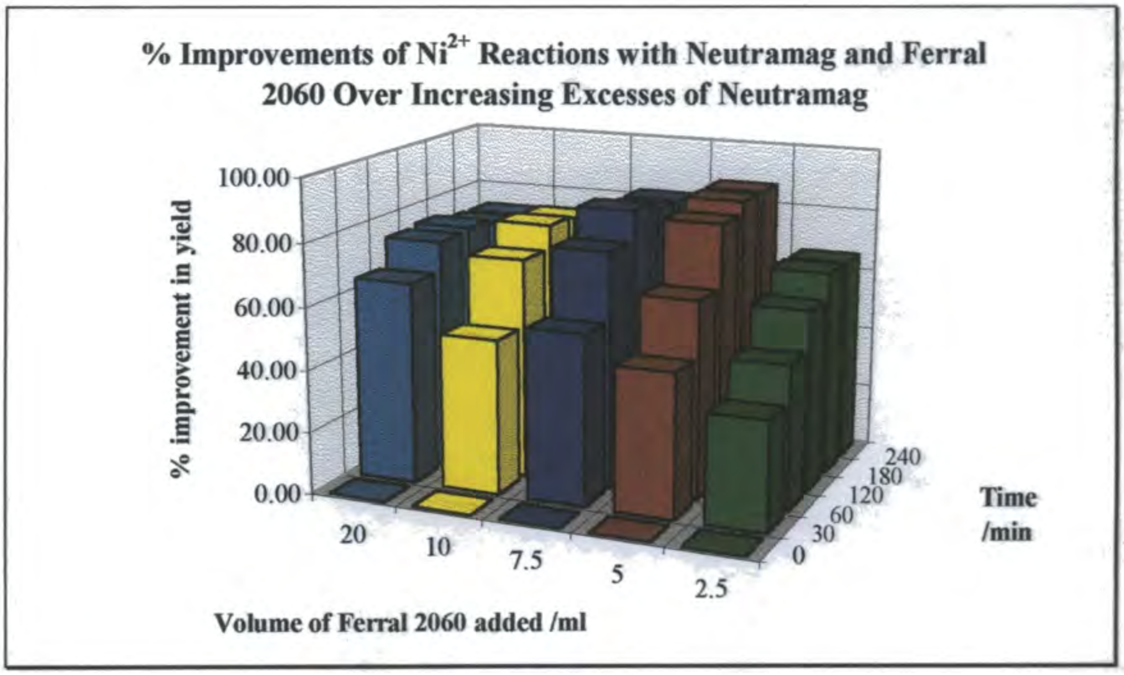

Figure 4.19

The use of Ferral Plus, a similar solution containing Al(III) and Fe(III) sulphates along with an extra component, a polyamine species, was tested, **section 4.3.1.6**. The results were very similar to the Ferral 2060 reaction. The inclusion of this other species would increase the price of the additive, a factor which must be kept to a minimum in industrial processes, so this was discarded in favour of the cheaper and equally effective Ferral 2060 solution.

4.5.3.2 Reactions with Zinc.

The same reactions were performed using Zn^{2+} solutions. 2.5ml, 5ml, 7.5ml, 10ml and 20ml aliquots of Ferral 2060 were used and the same amounts of Neutramag were used in control reactions.

Figure 4.20 - **Figure 4.24** show the concentrations of zinc achieved using Ferral 2060. Again the benefits of the use of Ferral 2060 can be plainly seen. The zinc reactions gave even better results than their nickel counterparts, although this was most evident in the earlier stages.

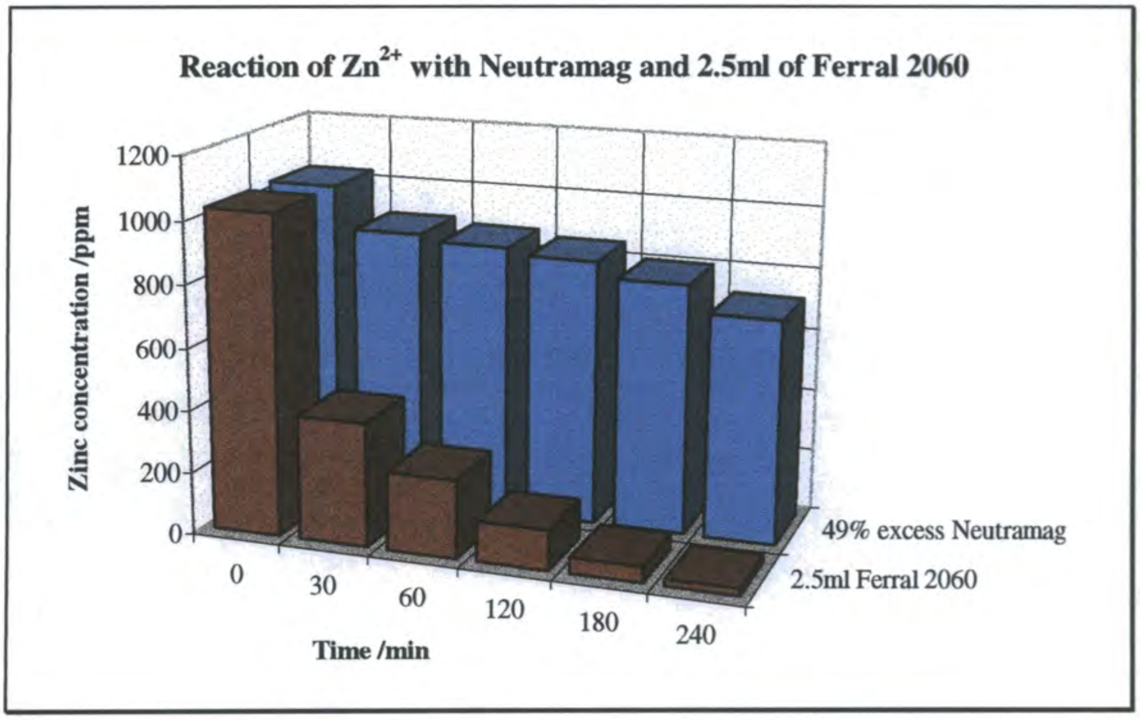

Figure 4.20

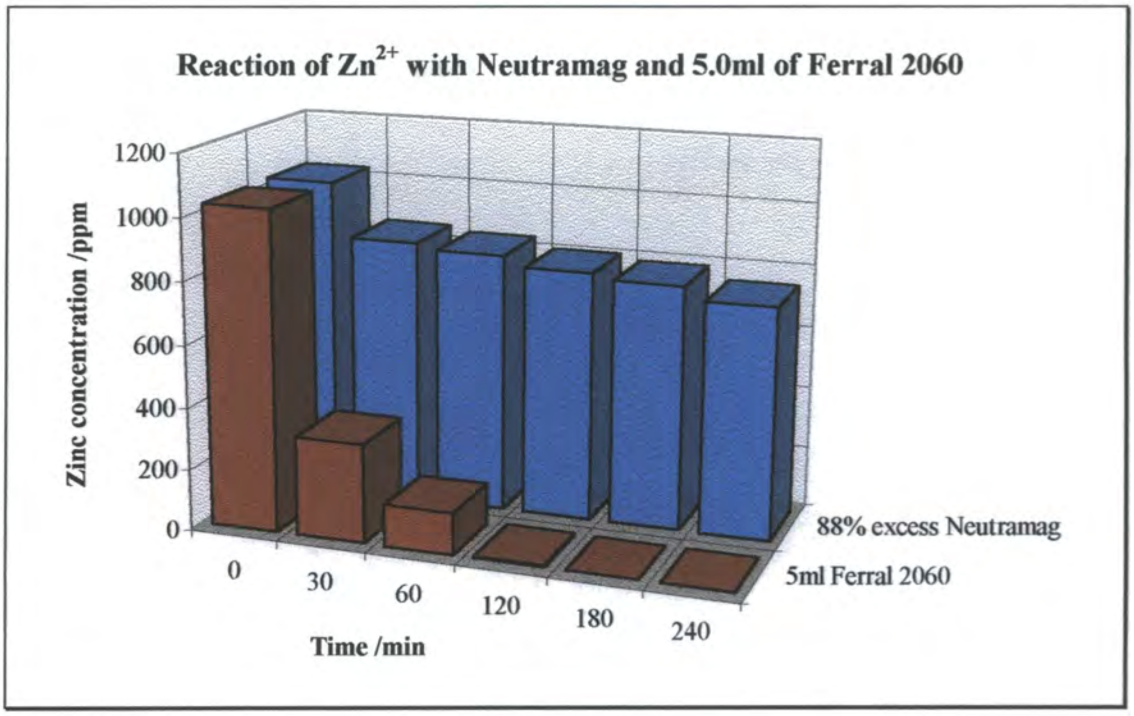

Figure 4.21

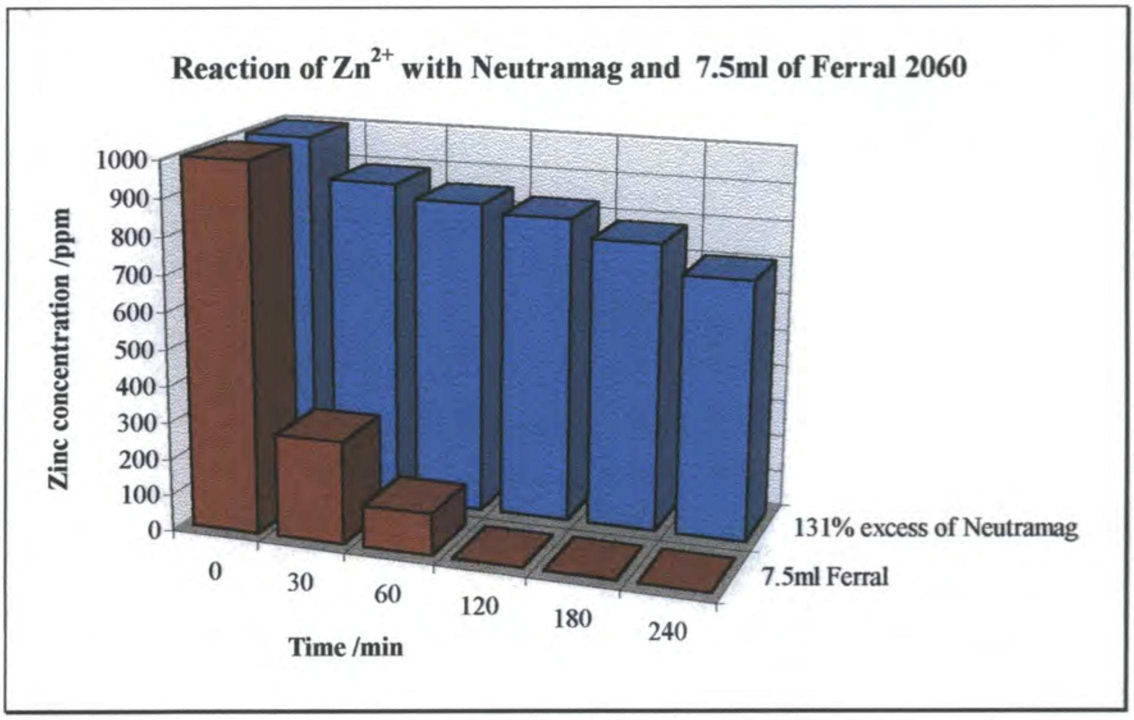

Figure 4.22

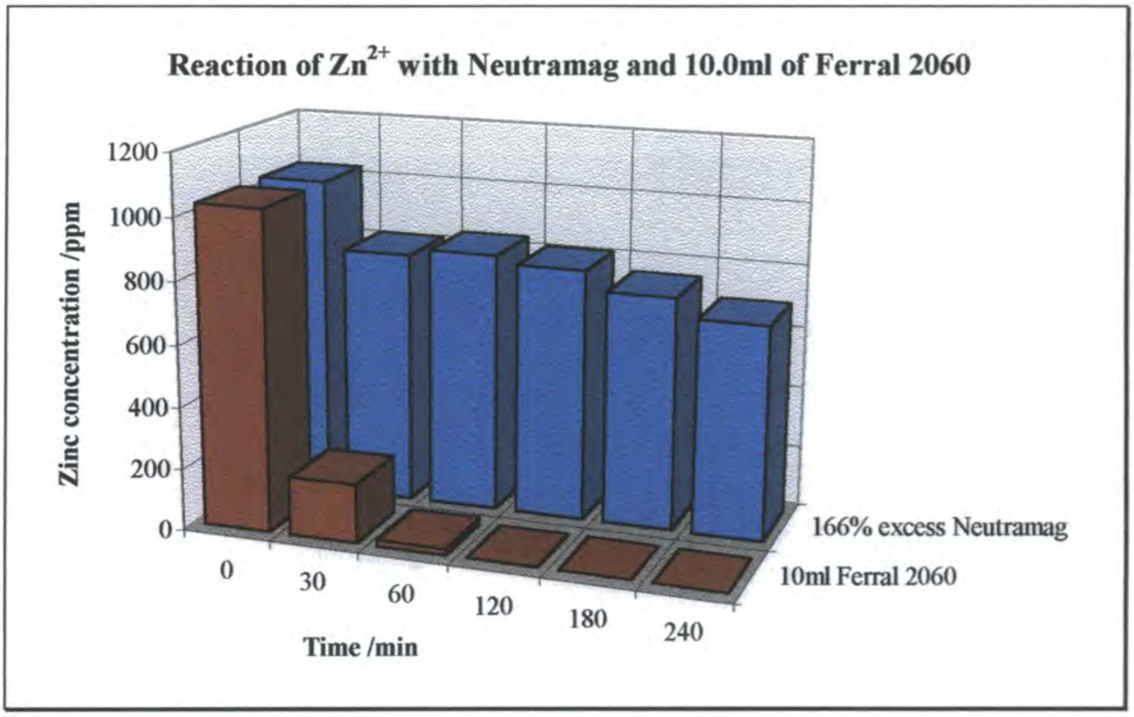

Figure 4.23

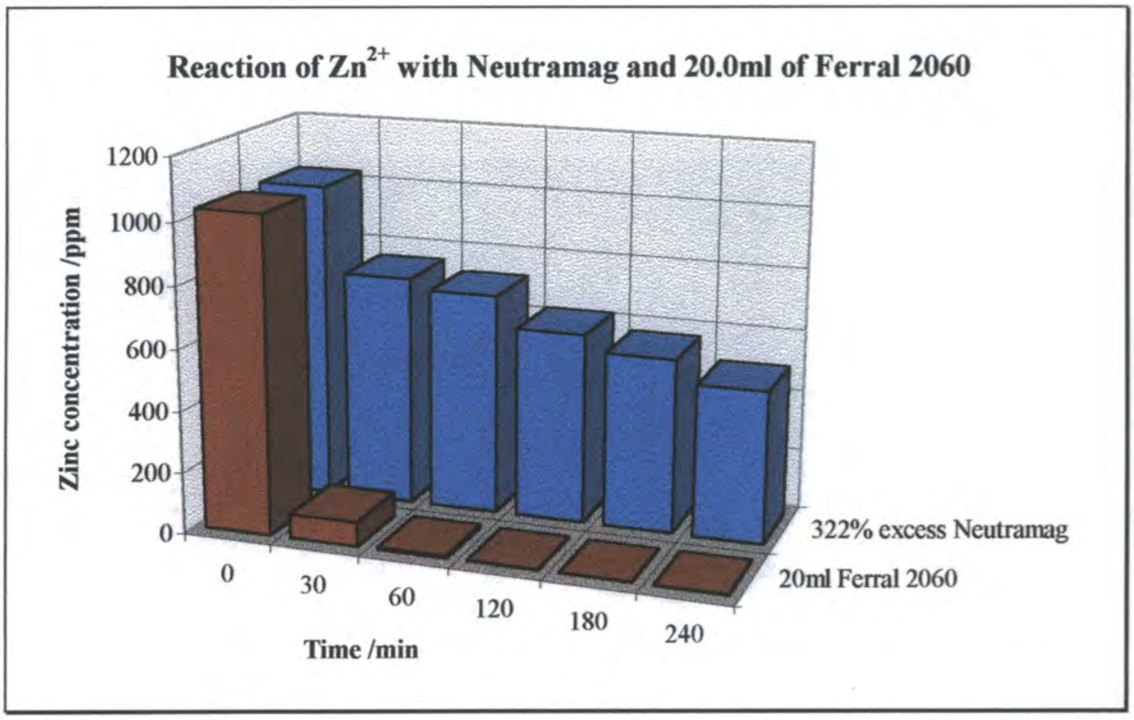

Figure 4.24

Figure 4.25 shows the percentage Zn^{2+} removed from these reactions with the addition of Ferral 2060 in the various amounts. It can be seen once more that the greater the addition of the M(III) solution the more Zn^{2+} is removed earlier in the reaction.

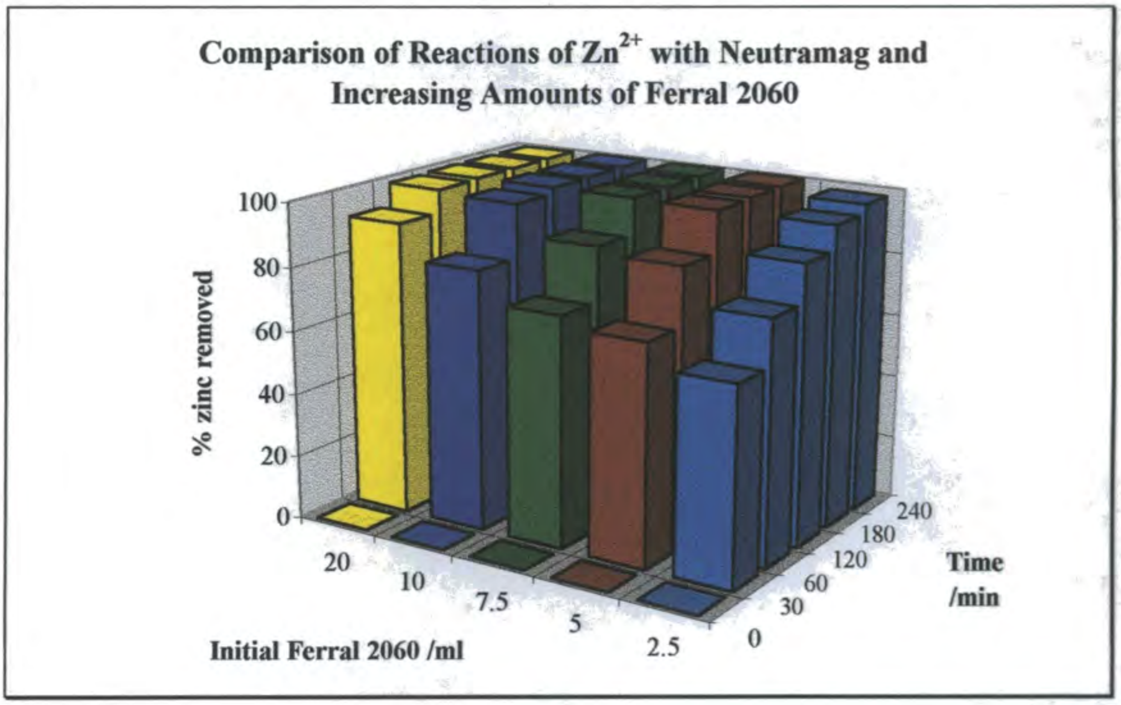

Figure 4.25

Figure 4.26 shows the amounts of zinc removed using just the larger excesses of Neutramag. As the excess increases so does the % removed for each time recorded. These removals are much lower than those seen with the addition of Ferral 2060, even though the % excess of Neutramag was much lower.

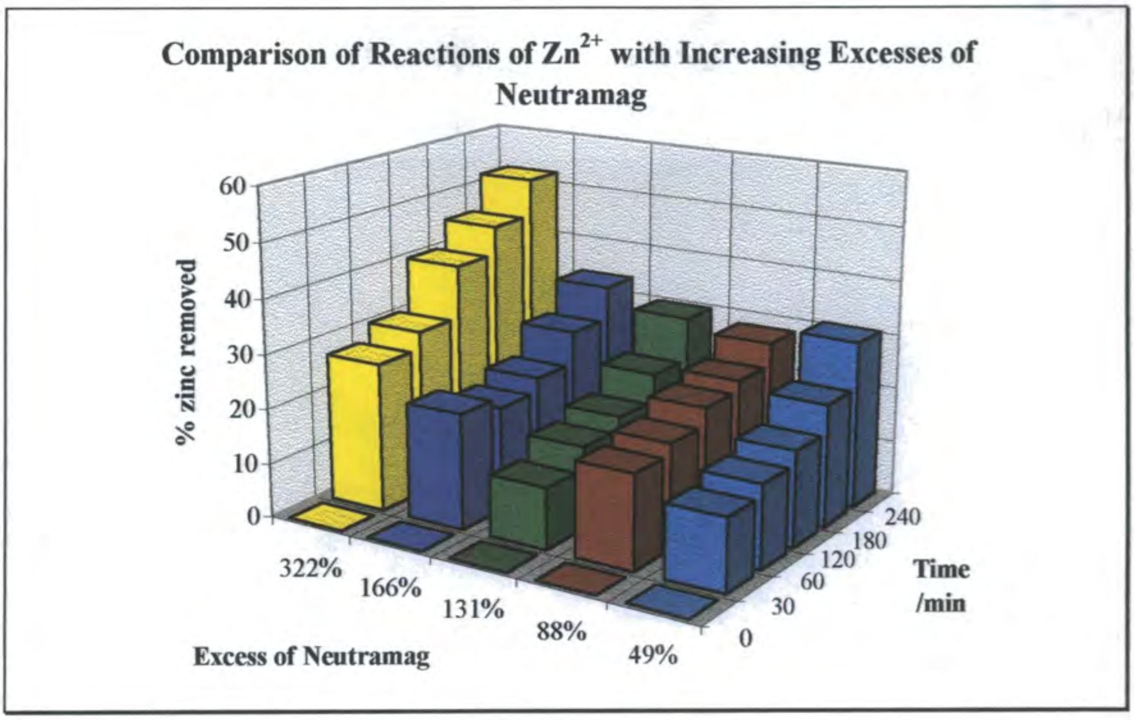

Figure 4.26

The percentage gained from the use of the Ferral 2060 solution is shown in **Figure 4.27**. These improvements were calculated by simply subtracting the % removed by excess Neutramag from the % removed using Ferral 2060. Again the greatest improvements were seen with the lower additions of Ferral. Although the % metal ion removals were greater for the higher additions, the larger excesses also gave better removals.

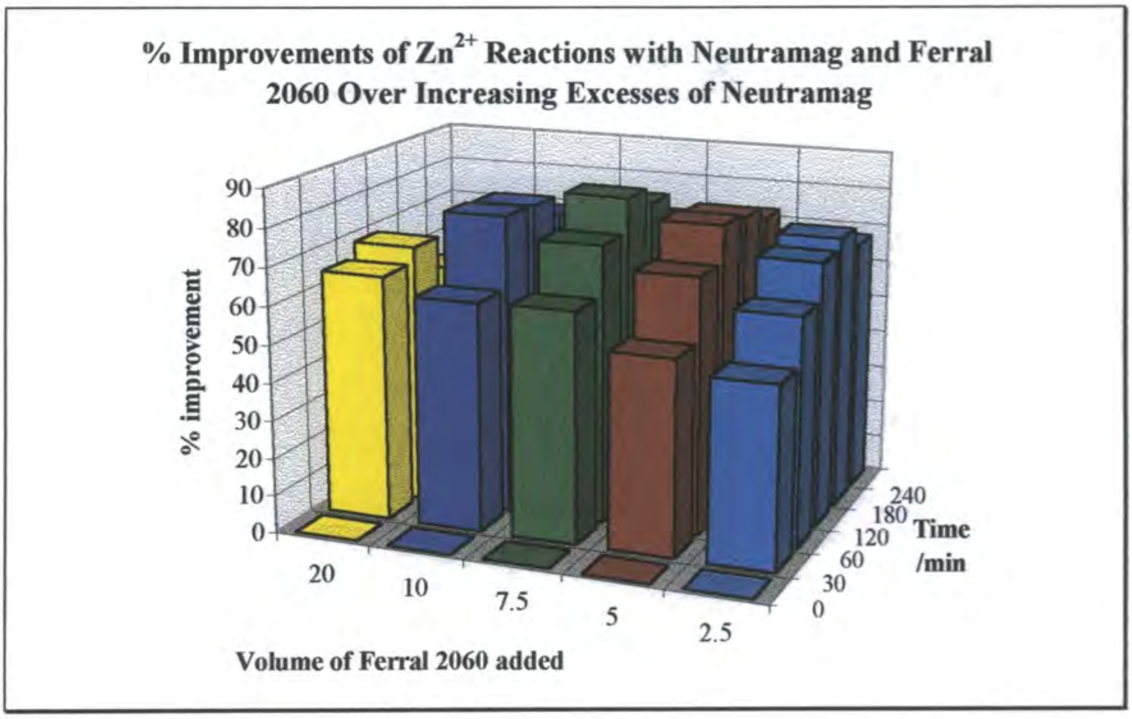

Figure 4.27

4.5.4 Reactions with Differing Filtrations.

Different filtration methods were used to see if any improvements in removal could be obtained from improvements in filtration. Initially a No.3 frit was to be used on its own, i.e. without the celite, but upon filtration the filtrate was found to be visibly cloudy. This result would not have been of any use and this filtration was abandoned.

The decrease in metal ion concentration using the celite indicated that there were solids present in the final reaction mixtures that were too small to be removed by the method used in the previous reactions. This meant that the %ages of precipitation quoted in those cases were in fact lower than those actually obtained but removal of the small particles was impossible.

Improvements in filtration may further reduce the final concentrations and longer periods of settling or the use of filter beds, both commonly used filtration methods in industrial systems, would show greater removals without utilising further reagents.

4.5.5 Conclusions.

Throughout the project one fact has become clear. Although there is always sufficient base present to completely precipitate the metal ions, in many cases this fails to occur. Not only is the concentration of metal ions too high in the final solution but the pH of the reaction mixture fails to reach the Neutramag buffer level of ~10.5. For the pH to remain so low throughout the reaction, a process other than the precipitation of $M(OH)_x$ must be occurring.

Ideally the reaction would proceed as follows. On addition of the Neutramag suspension to the metal ion solution the OH^- present in solution would react with the metal ions achieving some small amount of precipitation. As the bulk of the OH^- is tied up in the solid $Mg(OH)_2$ particles, in order for the reaction to continue, these solids must dissolve to free $OH^-_{(aq)}$. As the dissolved OH^- reacts with the metal ions, more $Mg(OH)_2$ should dissolve to maintain the equilibrium and the reaction should continue. The increasing OH^- concentration thus removes more metal ions until the reaction is said to be completed when the metal ion concentration reaches the desired level. If all the metal ions have been removed from the solution the remaining Neutramag will then achieve its own equilibrium at pH of ~10.5.

As this does not happen the Neutramag is somehow being prevented from dissolving as the buffer pH should be achieved even if it does not react with the metal ions. The reasons behind this remain unclear but several theories are discussed below.

In the reaction mixtures there are counter ions present that do not appear immediately involved in the precipitation process. The Mg^{2+}, NO^{3-} and/or SO_4^{2-} ions that come from Neutramag suspensions or metal ion solutions could also interact with the precipitating species rather than just allowing an exchange process to occur. While the precipitation reaction has been taken to be the production of insoluble $M(OH)_x$ species, the actual solids produced are likely to be more complicated than that. Metal hydroxides can also be thought of as hydrated metal oxides, e.g. $M^{(II)}O.H_2O$.

The presence of other ions in the mixture introduced the possibility of the formation of mixed metal oxides. The mixed oxides are known and exist in several forms, such as spinels or perovskites. Spinels ($A^{II}B^{III}{}_2O_4$) [19] and perovskites ($A^{II}B^{IV}O_3$) [20] are known for several of the ion combinations present in these reactions, $MgAl_2O_4$ is actually called spinel. Al^{3+} is known to form many spinel species and thus the idea that these mixed oxides would affect the reactions seems reasonable. In practice, however, the metal oxides remain distinct until subjected to high temps. The temperatures required to from these species are in excess of 800°C and so cannot be achieved in these aqueous systems. [21,22] While the precipitates may not be pure $M(OH)_x$, it seems very unlikely that it contains any of these mixed metal species.

The Neutramag dissolves in such a way that there is a region of high pH around the particles. [23] $M^{(II)}$ ions that are also present within this region will interact strongly with the OH– and precipitation will occur. The newly formed $M(OH)_2$ particles, still in close proximity to the larger $Mg(OH)_2$ solid. It is reasonable to suggest that the $M(OH)_2$ may adhere or adsorb to the $Mg(OH)_2$. [24] If this were to occur with sufficient frequency then a shell of insoluble $M(OH)_2$ may form around the $Mg(OH)_2$ and thus prevent it from undergoing any further dissolution and reaction. This would tie up any internal solid $Mg(OH)_2$ and effectively remove it from the reaction system.

This coating effect would seem to indicate that the precipitating hydroxide prefers to form on the $Mg(OH)_2$ particles rather than seed onto itself. With the addition of other species (Fe^{3+}, Al^{3+}) this effect does not seem to occur, all the metal ions being removed and higher pHs being achieved. This may indicate that the added metal ions provide even more preferred sites for precipitation so the build up around the Neutramag particles does not occur and the reaction can proceed to completion. This only works well when stoichiometric amount of the ions are added. Using less provides some improvement before the reaction stops again after there is no further available $M^{(III)}$ oxide to interact with.

In general these reactions gave very encouraging results. The treatment of Ni^{2+} and Zn^{2+} solutions was made possible without the use of large excesses of Neutramag. This reduction of the excess was one of the main aims behind the project.

The treatment of these metal ions still requires a relatively long time to proceed to completion. This reaction time is reduced with greater M(III) additions. The greater the addition of M(III), however, the larger the amount of Neutramag required to treat the solution. This system therefore becomes a trade off between rate of reaction needed against extra Neutramag added. As can be seen from the results, far greater benefits are obtained from the use of more Neutramag with M(III) than just more Neutramag.

As a general trend zinc was more receptive than nickel to the metal species, and Al^{3+} had the greatest influence on the M^{2+} ions.

Chapter 5

Studies on Reactions with Metal Oxides

5. Reactions with Metal Oxides.

5.1 Reactions with Re-using of Residues.

100ml of 10,000ppm Zn^{2+} solution (1.53×10^{-2}mol) were taken and made up to a volume of 1000ml with deionised water. This gave an initial concentration of 1000ppm Zn^{2+} (1.53×10^{-2}M). The pH was then measured. 6.2ml of the Neutramag slurry (1.53×10^{-2}mol) were added to the solution which gave no excess for full stoichiometric reaction. A sample of the reaction mixture was taken after 30 minutes and filtered to stop any further reaction. The reaction was stopped by filtration after 60 minutes. The concentrations of zinc remaining in the filtrates were determined by atomic absorption.

The residues from the 60 minute filtration were taken and dried. The reaction was repeated with the addition of a small quantity of the residue. These reactions were filtered and analysed as normal and the residues dried and used again in further reactions.

The results are shown in **Table 5.1**.

Table 5.1

Mass of residue added /g	**Readings at 0 minutes**	**Readings at 30 minutes**		**Readings at 60 minutes**	
	pH	**pH**	**Zn Concentration /ppm**	**pH**	**Zn Concentration /ppm**
None	4.02	7.73	1000	7.73	850
0.83	4.01	7.71	930	7.71	890
2.10	3.98	7.73	820	7.77	800
2.40	4.95	7.75	800	7.83	720

5.2 Reactions of Nickel.

5.2.1 Reactions with Aluminium Oxide.

100ml of 10,300ppm Ni^{2+} solution (1.75×10^{-2}mol) were taken and made up to a volume of 1000ml with deionised water. This gave an initial concentration of 1030ppm Ni^{2+} (1.75×10^{-2}M). The pH was then measured. 1.79g of Al_2O_3 (1.76×10^{-2}mol) were added to the solution, giving an Al_2O_3:Ni^{2+} ratio of 1:1. The pH was allowed to settle and then was measured again. 10.3ml of the Neutramag slurry (1.93×10^{-2}mol) were added to the solution which gave a 10% excess for full stoichiometric reaction. A sample of the reaction mixture was taken after 30 minutes and filtered to stop any further reaction. The reaction was stopped by filtration after 60 minutes. The concentrations of nickel remaining in the filtrates were determined by atomic absorption.

The reaction was repeated using increasing amounts of Al_2O_3. 3.58g (3.51×10^{-2}mol), 8.95g (8.78×10^{-2}mol) and 17.89g (1.75×10^{-1}mol) were used, equivalent to 2:1, 5:1 and 10:1 Al_2O_3:Ni^{2+} ratios respectively.

The results are shown in **Table 5.2**.

Table 5.2

Ratio Al_2O_3:Ni^{2+}	**Readings at 0 minutes**	**Readings at 30 minutes**		**Readings at 60 minutes**	
	pH	**pH**	**Nickel Concentration /ppm**	**pH**	**Nickel Concentration /ppm**
1:1	4.40	8.54	938	8.52	903
2:1	5.18	8.52	783	8.50	885
5:1	6.69	8.49	913	8.46	855
10:1	6.50	8.45	885	8.43	850

5.2.2 Reactions with Chromium(III) Oxide.

100ml of 10,300ppm Ni^{2+} solution (1.75×10^{-2}mol) were taken and made up to a volume of 1000ml with deionised water. This gave an initial concentration of 1030ppm Ni^{2+} (1.75×10^{-2}M). The pH was then measured. 2.67g of Cr_2O_3 (1.76×10^{-2}mol) were added to the solution, giving a Cr_2O_3:Ni^{2+} ratio of 1:1. The pH was allowed to settle and then was measured again. 10.3ml of the Neutramag slurry (1.93×10^{-2}mol) were added to the solution which gave a 10% excess for full stoichiometric reaction. A sample of the reaction mixture was taken after 30 minutes and filtered to stop any further reaction. The reaction was stopped by filtration after 60 minutes. The concentrations of nickel remaining in the filtrates were determined by atomic absorption.

The reaction was repeated using increasing amounts of Cr_2O_3. 5.33g (3.51×10^{-2}mol), 13.34g (8.78×10^{-2}mol) and 26.67g (1.75×10^{-1}mol) were used, equivalent to 2:1, 5:1 and 10:1 Cr_2O_3:Ni^{2+} ratios respectively.

The results are shown in **Table 5.3**.

Table 5.3

Ratio Cr_2O_3:Ni^{2+}	**Readings at 0 minutes**	**Readings at 30 minutes**		**Readings at 60 minutes**	
	pH	**pH**	**Nickel Concentration /ppm**	**pH**	**Nickel Concentration /ppm**
1:1	4.03	8.37	953	8.37	940
2:1	4.11	8.45	940	8.45	915
5:1	4.28	7.91	943	7.90	920
10:1	4.78	8.47	913	8.46	895

5.2.3 Reactions with Titanium(IV) Oxide.

100ml of 9,700ppm Ni^{2+} solution (1.75×10^{-2}mol) were taken and made up to a volume of 1000ml with deionised water. This gave an initial concentration of 970ppm Ni^{2+} (1.65×10^{-2}M). The pH was then measured. 1.32g of TiO_2 (1.65×10^{-2}mol) were added to the solution, giving a TiO_2:Ni^{2+} ratio of 1:1. The pH was allowed to settle and then was measured again. 9.7ml of the Neutramag slurry (1.82×10^{-2}mol) were added to the solution which gave a 10% excess for full stoichiometric reaction. A sample of the reaction mixture was taken after 30 minutes and filtered to stop any further reaction. The reaction was stopped by filtration after 60 minutes. The concentrations of nickel remaining in the filtrates were determined by atomic absorption.

The reaction was repeated using increasing amounts of TiO_2. 2.64g (3.31×10^{-2}mol), 6.60g (8.26×10^{-2}mol) and 13.20g (1.65×10^{-1}mol) were used, equivalent to 2:1, 5:1 and 10:1 TiO_2:Ni^{2+} ratios respectively.

The results are shown in **Table 5.4**.

Table 5.4

Ratio TiO_2:Ni^{2+}	Readings at 0 minutes	Readings at 30 minutes		Readings at 60 minutes	
	pH	pH	Nickel Concentration /ppm	pH	Nickel Concentration /ppm
1:1	6.23	8.32	925	8.45	950
2:1	6.35	8.46	645	8.47	680
5:1	6.51	8.57	915	8.59	885
10:1	6.77	8.59	915	8.58	730

5.2.4 Reactions Over 4 Hours.

100ml of 9,500ppm Ni^{2+} solution (1.62×10^{-2}mol) were taken and made up to a volume of 1000ml with deionised water. This gave an initial concentration of 950ppm Ni^{2+} (1.62×10^{-2}M). The pH was then measured. 9.5ml of the Neutramag slurry (1.78×10^{-2}mol) were added to the solution which gave a 10% excess for full stoichiometric reaction. The reaction was stopped by filtration after 240 minutes. The concentrations of nickel remaining in the filtrates were determined by atomic absorption.

The reaction was repeated using different metal oxides. 8.25g (8.09×10^{-2}mol) of Al_2O_3, 12.30g (8.09×10^{-2}mol) of Cr_2O_3, and 6.46g (8.09×10^{-2}mol) of TiO_2 were used, giving oxide:Ni^{2+} ratios of 5:1.

The results are shown in **Table 5.5**.

Table 5.5

Metal Oxide	**Initial pH**	**Final pH**	**Nickel Concentration /ppm**	**% Nickel Removed**
None	4.00	8.21	893	6.0
Al_2O_3	3.99	8.34	858	9.7
Cr_2O_3	4.01	8.67	898	5.5
TiO_2	3.96	8.63	843	11.3

5.2.5 Reaction with Iron(III) Phosphate.

100ml of 10,000ppm Ni^{2+} solution (1.70×10^{-2}mol) were taken and made up to a volume of 1000ml with deionised water. This gave an initial concentration of 1000ppm Ni^{2+} (1.70×10^{-2}M). The pH was then measured. 3.80g of $FePO_4.4H_2O$ (1.70×10^{-2}mol) were added to the solution, giving a $FePO_4$:Ni^{2+} ratio of 1:1. The pH was allowed to settle and then was measured again. 7.7ml of the Neutramag slurry (1.87×10^{-2}mol) were added to the solution which gave a 10% excess for full stoichiometric reaction. A sample of the reaction mixture was taken after 30 minutes and filtered to stop any further reaction. The reaction was stopped by filtration after 60 minutes. The concentrations of nickel remaining in the filtrates were determined by atomic absorption.

The results are shown in **Table 5.6**.

Table 5.6

Ratio $FePO_4$:Ni^{2+}	Readings at 0 minutes	Readings at 30 minutes		Readings at 60 minutes	
	pH	pH	Nickel Concentration /ppm	pH	Nickel Concentration /ppm
1:1	6.82	8.47	895	8.49	890

5.3 Reactions of Zinc.

5.3.1 Reactions with Aluminium Oxide.

100ml of 10,750 Zn^{2+} solution (1.64×10^{-2}mol) were taken and made up to a volume of 1000ml with deionised water. This gave an initial concentration of 1075ppm Zn^{2+} (1.64×10^{-2}M). The pH was then measured. 1.67g of Al_2O_3 (1.64×10^{-2}mol) were added to the solution, giving an Al_2O_3:Zn^{2+} ratio of 1:1. The pH was allowed to settle and then was measured again. 9.6ml of the Neutramag slurry (1.81×10^{-2}mol) were added to the solution which gave a 10% excess for full stoichiometric reaction. A sample of the reaction mixture was taken after 30 minutes and filtered to stop any further reaction. The reaction was stopped by filtration after 60 minutes. The concentrations of zinc remaining in the filtrates were determined by atomic absorption.

The reaction was repeated using increasing amounts of Al_2O_3. 3.35g (3.26×10^{-2}mol), 8.38g (8.22×10^{-2}mol) and 16.76g (1.64×10^{-1}mol) were used, equivalent to 2:1, 5:1 and 10:1 Al_2O_3:Zn^{2+} ratios respectively.

The results are shown in **Table 5.7**.

Table 5.7

Ratio Al_2O_3:Zn^{2+}	**Readings at 0 minutes**	**Readings at 30 minutes**		**Readings at 60 minutes**	
	pH	**pH**	**Zinc Concentration /ppm**	**pH**	**Zinc Concentration /ppm**
1:1	4.70	7.50	985	7.70	958
2:1	5.42	7.50	945	7.65	928
5:1	6.32	7.48	935	7.58	883
10:1	6.84	7.43	920	7.61	863

5.3.2 Reactions with Chromium(III) Oxide.

100ml of 9,750 Zn^{2+} solution (1.48×10^{-2}mol) were taken and made up to a volume of 1000ml with deionised water. This gave an initial concentration of 975ppm Zn^{2+} (1.48×10^{-2}M). The pH was then measured. 2.27g of Cr_2O_3 (1.49×10^{-2}mol) were added to the solution, giving a Cr_2O_3:Zn^{2+} ratio of 1:1. The pH was allowed to settle and then was measured again. 8.7ml of the Neutramag slurry (1.64×10^{-2}mol) were added to the solution which gave a 10% excess for full stoichiometric reaction. A sample of the reaction mixture was taken after 30 minutes and filtered to stop any further reaction. The reaction was stopped by filtration after 60 minutes. The concentrations of zinc remaining in the filtrates were determined by atomic absorption.

The reaction was repeated using increasing amounts of Cr_2O_3. 4.53g (2.98×10^{-2}mol), 11.33g (7.45×10^{-2}mol) and 22.67g (1.49×10^{-1}mol) were used, equivalent to 2:1, 5:1 and 10:1 Cr_2O_3:Zn^{2+} ratios respectively.

The results are shown in **Table 5.8**.

Table 5.8

Ratio Cr_2O_3:Zn^{2+}	**Readings at 0 minutes**	**Readings at 30 minutes**		**Readings at 60 minutes**	
	pH	**pH**	**Zinc Concentration /ppm**	**pH**	**Zinc Concentration /ppm**
1:1	4.15	7.04	933	7.07	905
2:1	4.19	7.10	925	7.10	895
5:1	4.33	7.12	900	7.08	875
10:1	4.58	7.14	888	7.11	850

5.3.3 Reactions with Titanium(IV) Oxide.

100ml of 9,500ppm Zn^{2+} solution (1.45×10^{-2}mol) were taken and made up to a volume of 1000ml with deionised water. This gave an initial concentration of 950ppm Zn^{2+} (1.45×10^{-2}M). The pH was then measured. 1.16g of TiO_2 (1.45×10^{-2}mol) were added to the solution, giving a TiO_2:Zn^{2+} ratio of 1:1. The pH was allowed to settle and then was measured again. 8.5ml of the Neutramag slurry (1.60×10^{-2}mol) were added to the solution which gave a 10% excess for full stoichiometric reaction. A sample of the reaction mixture was taken after 30 minutes and filtered to stop any further reaction. The reaction was stopped by filtration after 60 minutes. The concentrations of nickel remaining in the filtrates were determined by atomic absorption.

The reaction was repeated using increasing amounts of TiO_2. 2.32g (2.90×10^{-2}mol), 5.80g (7.26×10^{-2}mol) and 11.61g (1.45×10^{-1}mol) were used, equivalent to 2:1, 5:1 and 10:1 TiO_2:Ni^{2+} ratios respectively.

The results are shown in **Table 5.9**.

Table 5.9

Ratio TiO_2:Zn^{2+}	**Readings at 0 minutes**	**Readings at 30 minutes**		**Readings at 60 minutes**	
	pH	**pH**	**Zinc Concentration /ppm**	**pH**	**Zinc Concentration /ppm**
1:1	4.17	7.45	850	7.56	812
2:1	4.25	7.63	793	7.70	750
5:1	4.65	7.54	753	7.52	730
10:1	4.95	7.55	705	7.65	688

5.3.4 Reactions Over 4 Hours.

100ml of 9,500ppm Zn^{2+} solution (1.45×10^{-2}mol) were taken and made up to a volume of 1000ml with deionised water. This gave an initial concentration of 950ppm Zn^{2+} (1.45×10^{-2}M). The pH was then measured. 8.5ml of the Neutramag slurry (1.60×10^{-2}mol) were added to the solution which gave a 10% excess for full stoichiometric reaction. The reaction was stopped by filtration after 240 minutes. The concentration of zinc remaining in the filtrate was determined by atomic absorption.

The reaction was repeated using different metal oxides. 7.41g (7.26×10^{-2}mol) of Al_2O_3, 11.04g (7.26×10^{-2}mol) of Cr_2O_3, and 5.80g (7.26×10^{-2}mol) of TiO_2 were used, giving oxide:Ni^{2+} ratios of 5:1.

The results are shown in **Table 5.10**.

Table 5.10

Metal Oxide	**Initial pH**	**Final pH**	**Zinc Concentration /ppm**	**% Zinc Removed**
None	3.90	7.28	763	19.7
Al_2O_3	5.73	7.96	785	17.4
Cr_2O_3	4.06	7.36	748	17.4
TiO_2	4.02	7.96	768	19.2

5.4 Discussion.

5.4.1 Introduction.

Treatment of metal ions with M(III) solutions, either singly or as the dual metal ions solution Ferral, had been shown to be very effective, **Chapter 4**. Far higher % metal ion removals were obtained than with large excesses of Neutramag. The drawback to the use of these reagents was the need to treat them with further Neutramag. Metal(III) ions require $^3/_2$ again the amount of Neutramag that M(II) ions do, on top of that required to treat the effluent species. As the effects of the M(III) solutions decrease with lower additions and generally require equivalent amounts relative to the effluent species, this can amount to a large increase in Neutramag usage.

In the reaction with M(III) ions, the M(III) species, which are much less soluble, precipitate out first. After this, when the pH has increased further, the other ions will start to precipitate. At this point the precipitation is affected by the M(III) species, which are now present as solids. If the precipitation is improved by interaction with a solid it was considered possible that the effluents could be treated with addition of solids. These solid species would not require the extra Neutramag to precipitate them when added to the effluents.

5.4.2 Re-using of Residues.

The first set of reactions performed with solid additives used a very simple process, **section 5.1**. One reaction was treated with Neutramag as normal. The residue from the final filtration of this reaction was dried in air and finely ground using a pestle and mortar. Some of this solid was added to a further reaction, and the residue from this reactions final filtration was dried, ground and added to another. This process was repeated several times and the results showed that, with increasing amounts of this oxide mixture, improved removals were obtained, **Figure 5.1**.

The residues added in this process contained not only oxide species but unreacted Neutramag solids. This would make the process more efficient and hence beneficial to an industrial process.

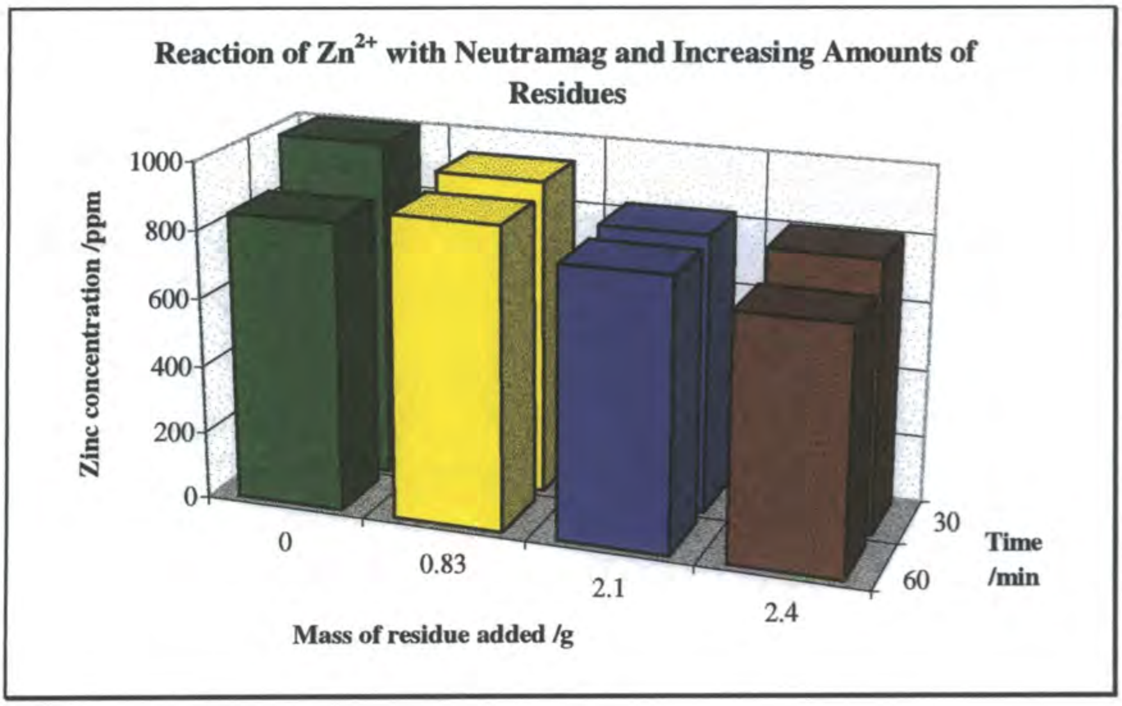

Figure 5.1

These metal ion removals were not as good as the ones seen with the use of solution additives, **Chapter 4**. This is probably due to two factors. Firstly, the species used in the solution reactions were easily precipitated, whereas Zn^{2+} is relatively hard to treat and as such seemed to have little beneficial effect in the treatments. The easier the ion is to precipitate, the greater the effect appears to be. The second point is that the solid added would be present as much larger particles, with a lower total surface area, than the solids precipitated *in situ*.

However, as the additive in this case would be freely available from the treatments performed, a small increase per addition could be built up to a much larger level if large enough quantities of residue were used. A simple method of achieving this would be to dispose of the residue from the reaction vessel less often.

5.4.3 Reactions of Nickel.

The next step in these reactions was the use of known metal(III) oxides. Known molar quantities of oxide were added and the changes in the reaction analysed, **section 5.2**.

The first of these reactions used Al_2O_3. This is the dehydrated from of $Al(OH)_3$ which precipitates in the Al^{3+} solution reactions. The alumina was added in a 1:1 molar ratio, then in increasing ratios of 2:1, 5:1 and 10:1, **section 5.2.1**.

Small improvements were seen with the 1:1 reactions, but again these were not as good as the improvements seen in the solution reactions. Increasing the amount of oxide added increased these improvements but even with a 10:1 excess only ~10% extra was removed, **Figure 5.2**.

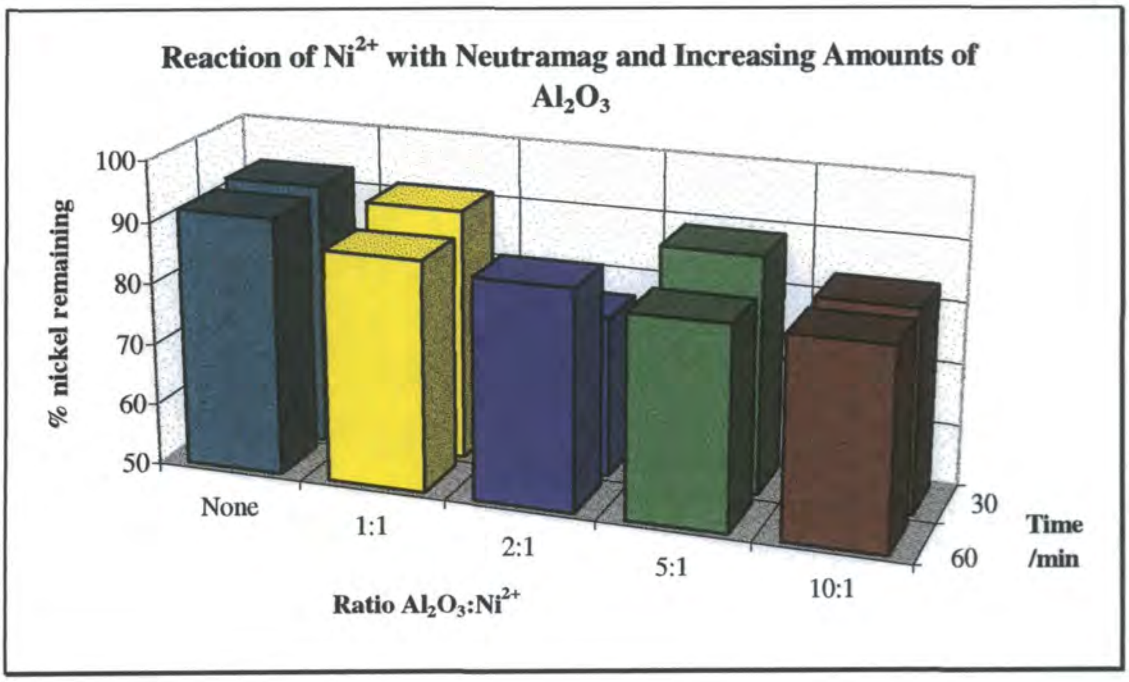

Figure 5.2

Using Cr_2O_3 instead of Al_2O_3 gave even smaller improvements, **section 5.2.2** and **Figure 5.3**.

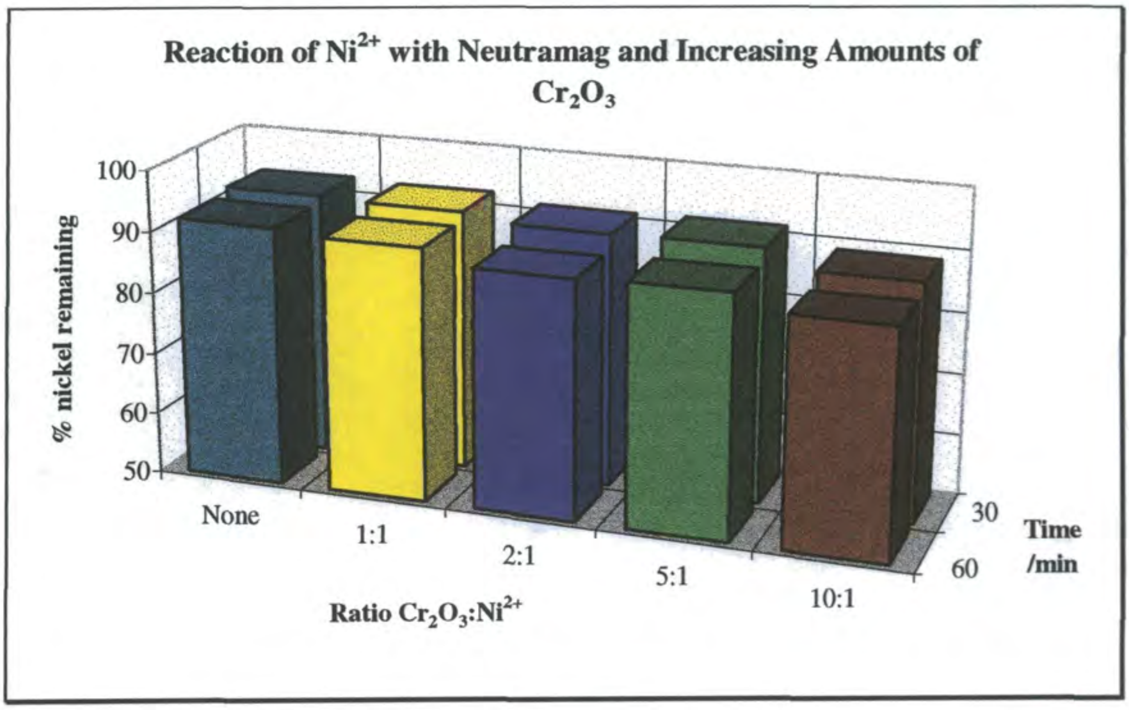

Figure 5.3

Exchanging the additive for a M(IV) oxide, TiO_2, gave slightly better metal ion removal, **section 5.2.3**, although still nowhere near as high as the solution reactions, **Figure 5.4**. The large apparent decrease for the 2:1 reaction is almost certainly an error when compared with the other results.

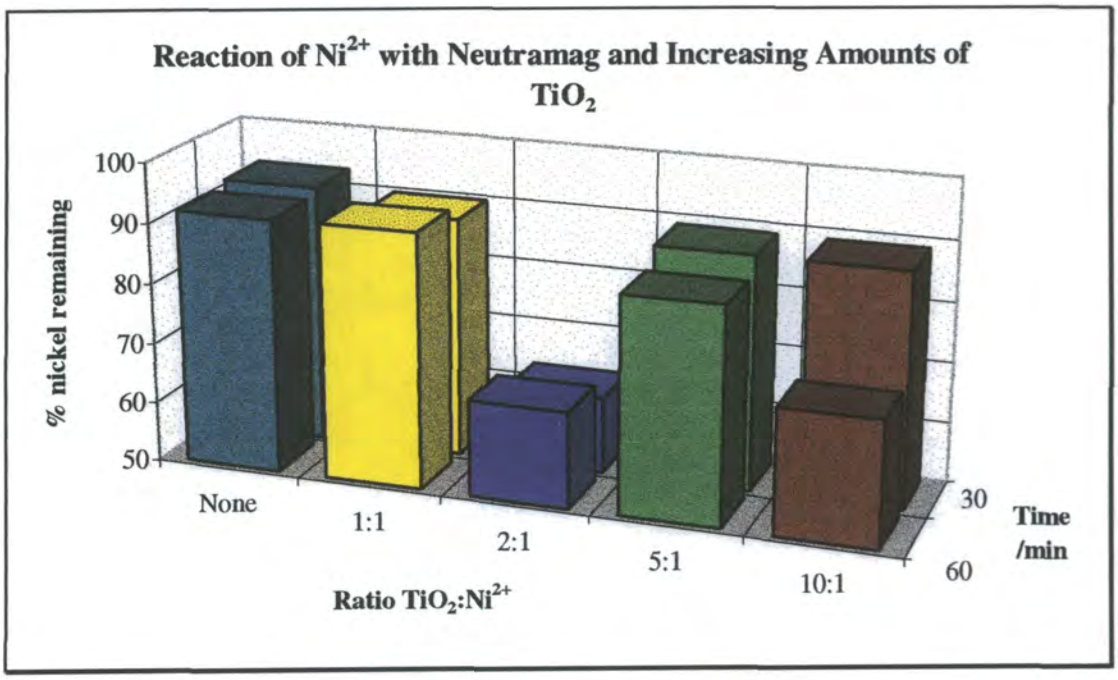

Figure 5.4

Comparison of these reactions seemed to show that Al_2O_3 and TiO_2 gave the best results, **Figure 5.5**.

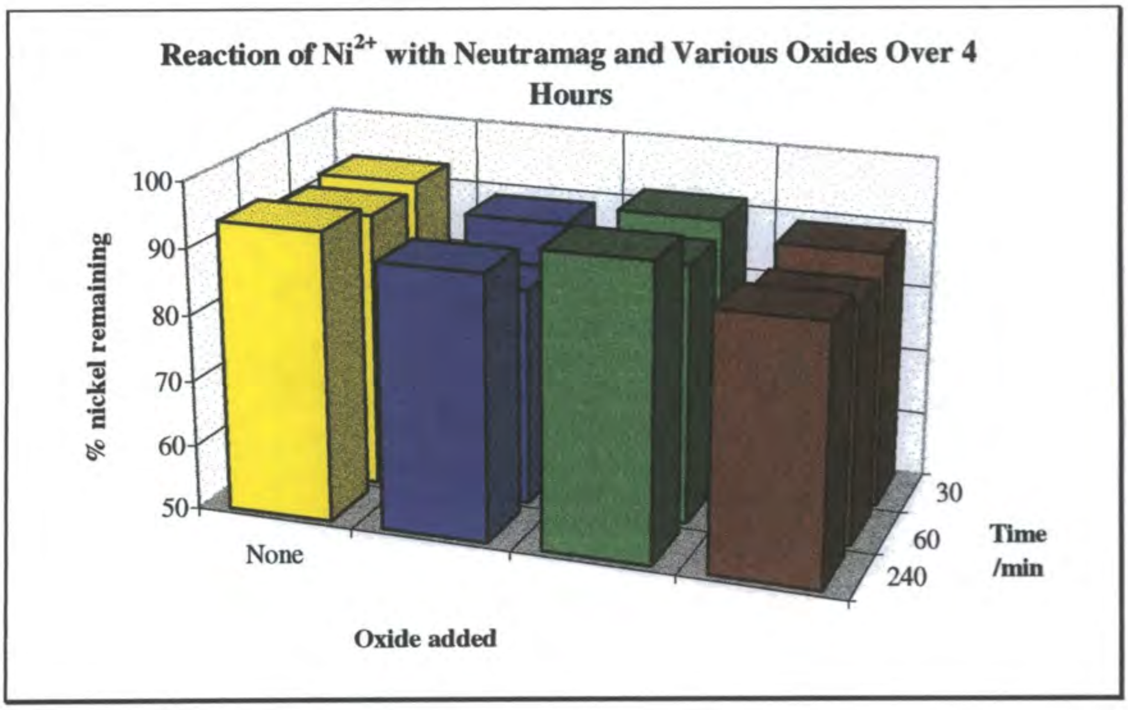

Figure 5.5

Increasing the reaction time to 4 hours did not increase the metal ion removal by much; only the addition of further solid oxide seemed to achieve this, **section 5.2.4**.

A single reaction with a different M(III) species was attempted. $FePO_4$ was reacted in a similar manner at a 1:1 molar ratio. In comparison, the result was promising, giving similar results to the 1:1 Al_2O_3 reaction, **section 5.2.5** and **Figure 5.6**.

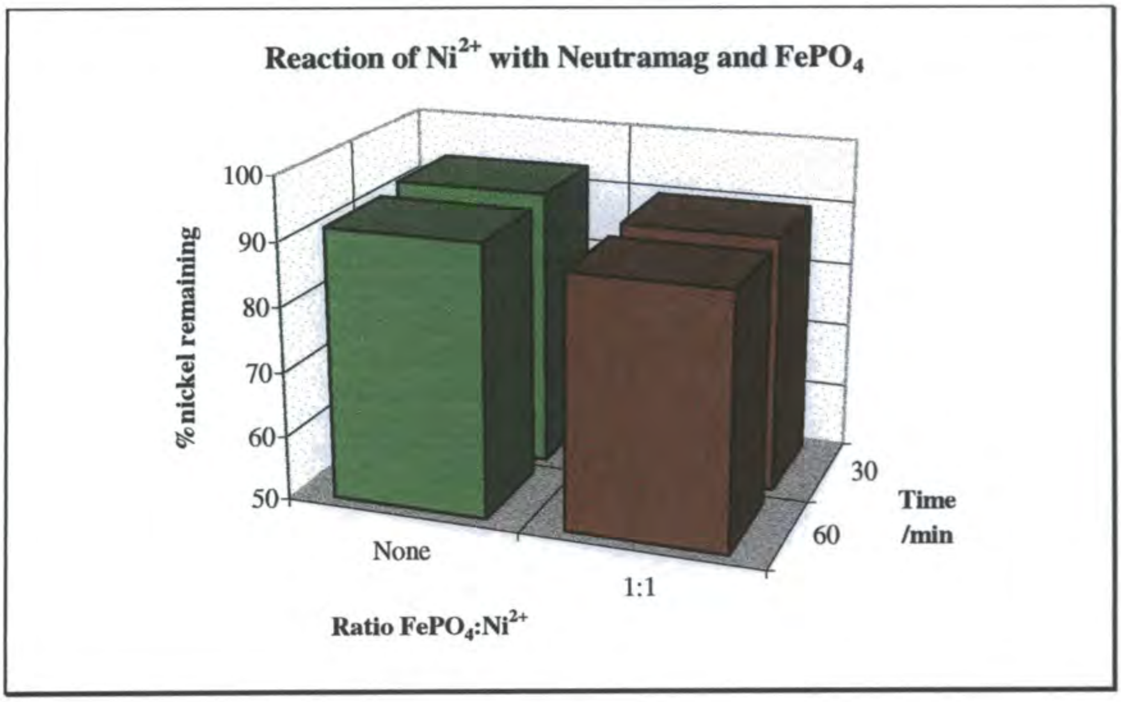

Figure 5.6

The use of phosphate is not as useful in an industrial process. Metal oxides such as Al_2O_3, TiO_2 and Fe_2O_3 are cheap to acquire and utilise in large quantities. $FePO_4$ is more expensive, and therefore its benefits would have to be more sizeable to offset this extra expenditure.

5.4.4 Reactions of Zinc.

Reactions were also performed on Zn^{2+} solutions with these oxides, **section 5.3**. Zn^{2+} had reacted slightly more favourably than Ni^{2+} with the M(III) solutions and it was hoped that this trend would be repeated here.

Al_2O_3 gave some improvement but no greater than that seen with the Ni^{2+} reactions, **section 5.3.1** and **Figure 5.7**.

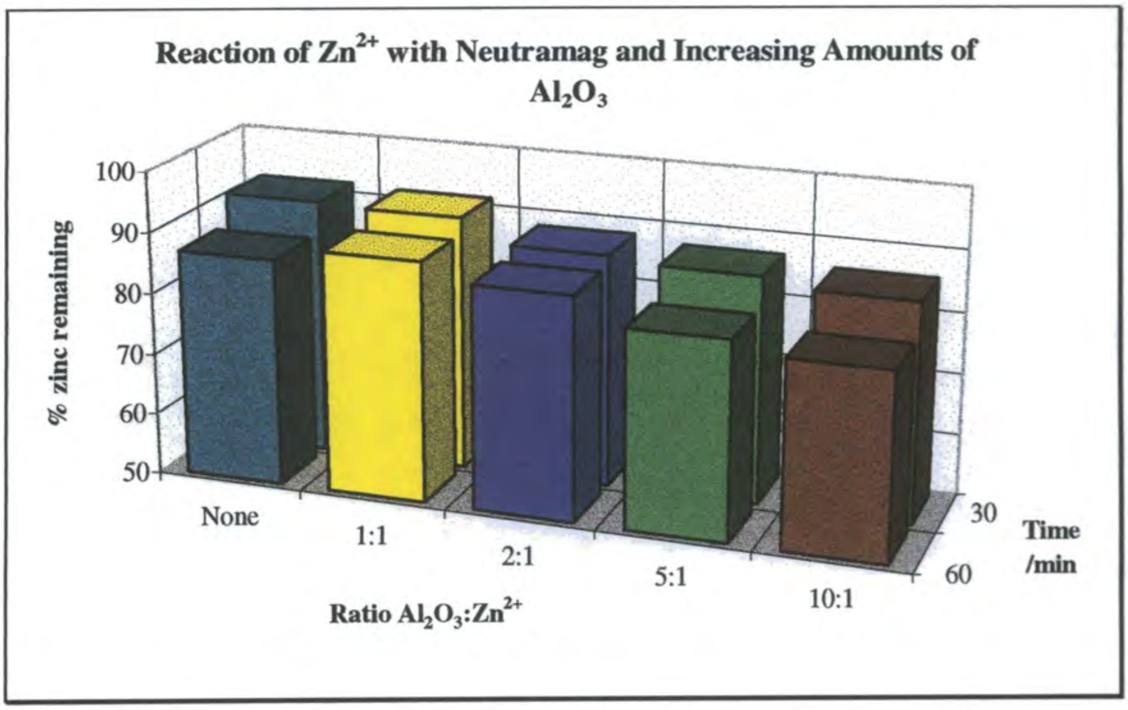

Figure 5.7

Exchanging the oxide for Cr_2O_3 did give improvement over Al_2O_3 in this case, **section 5.3.2** and **Figure 5.8**. This improvement was greater at the lower additions but less noticeable when the 10:1 ratio was reached.

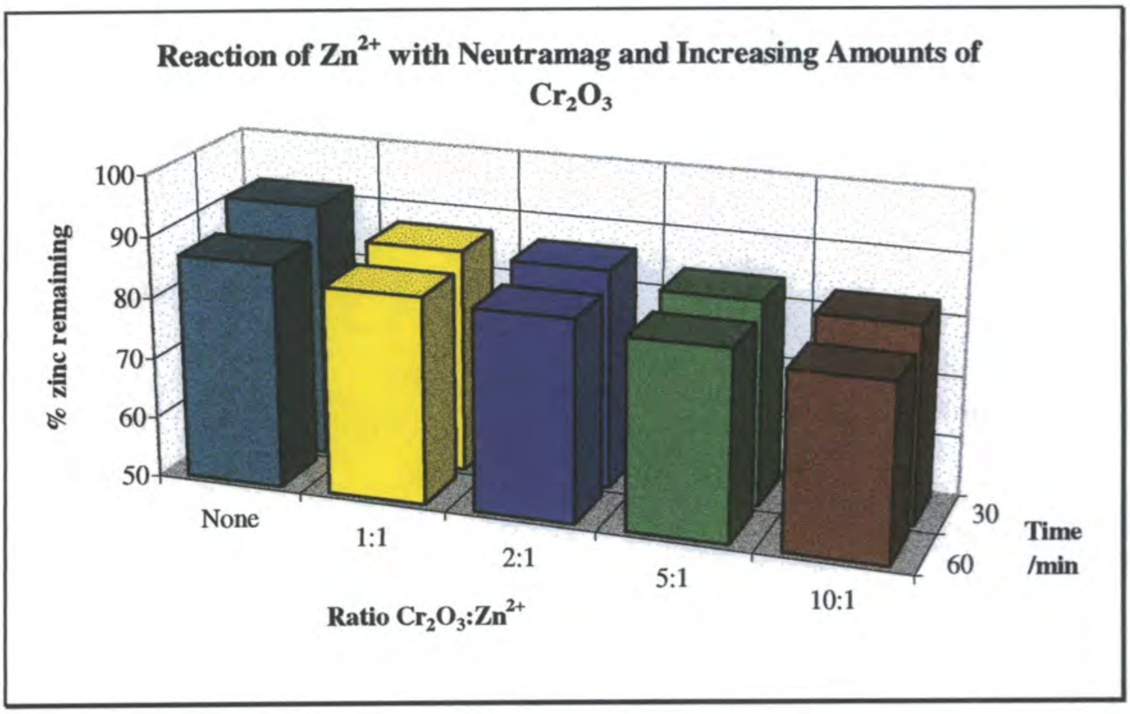

Figure 5.8

Further improvement was seen with TiO_2, an extra 15% being removed in the 10:1 reaction, **section 5.3.3** and **Figure 5.9**.

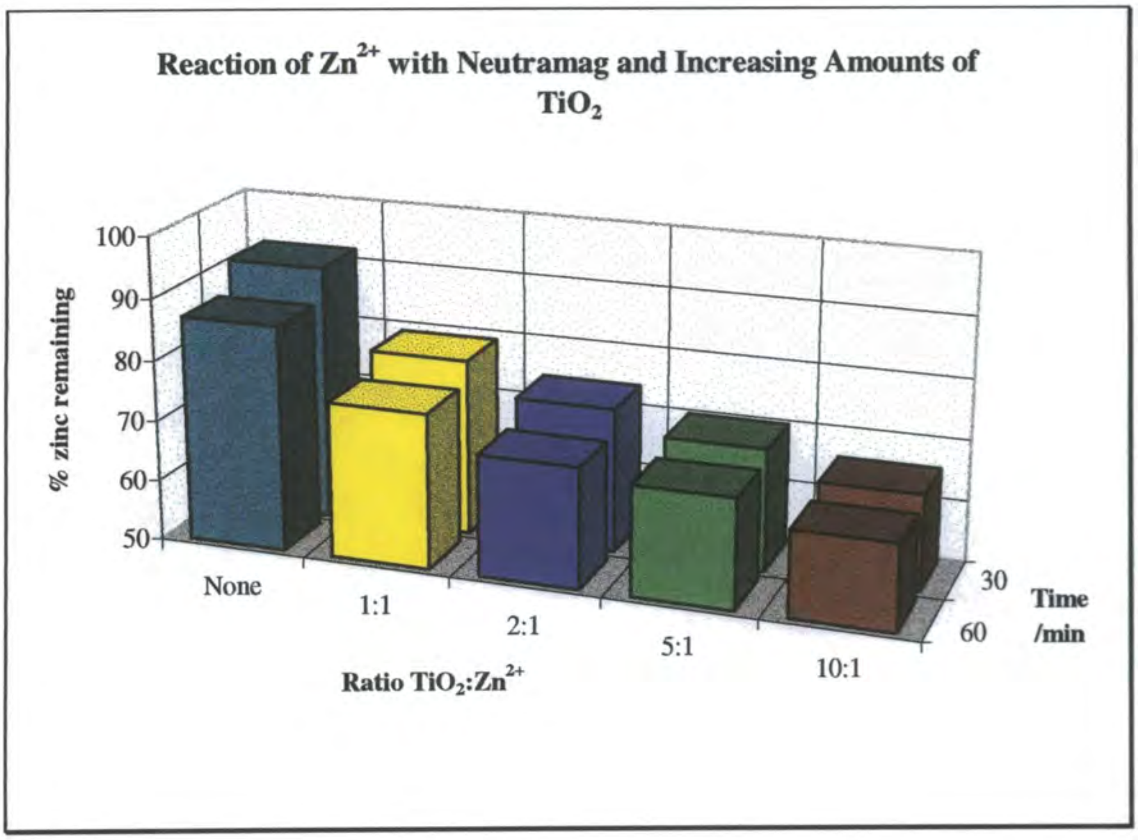

Figure 5.9

Allowing the reactions to proceed for longer, 4 hours, showed different results from the Ni^{2+} reactions, **Figure 5.10**. Ni^{2+} did not show any improvement with increased time but each of the additions to Zn^{2+} gave similar results, between 15 and 20% removal, **section 5.3.4**. The control reaction also achieved ~20% metal ion removal so this sees to be the norm and the additions are only increasing the reactivity in the shorter times.

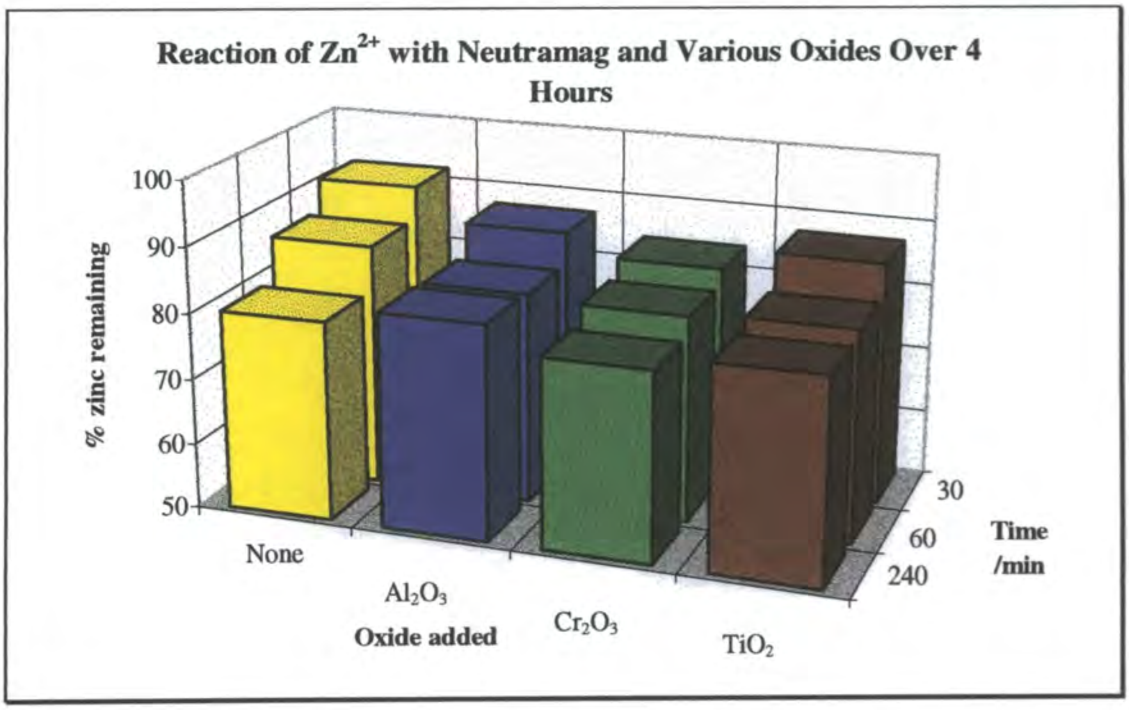

Figure 5.10

5.5 Conclusions.

Although some improvement in the reactions was seen it was not on the same scale as with the M(III) solution additions, and far more additive was required to attain any significant increase in reaction. The smaller improvements in metal ion removal with the addition of the oxides can be attributed to the larger particle size compared to the newly precipitated hydroxides. The fact that the species are largely dehydrated, oxides as opposed to hydroxides, may also be a contributing factor.

Again the components are present to form mixed metal oxide species, $CaTiO_3$ being a known perovskite and could be analogous to species like $NiTiO_3$ and $ZnTiO_3$. However the conditions are not sufficiently harsh, temperatures in excess of 800°C being required to form the mixed metal species.

Recycling of the residues back into the reactions from previous treatments could enable this method to be more efficiently utilised. Not only would the benefits from the M(III) species become available, but the unreacted Neutramag would not be wasted and disposed of with oxide residues. This recycling process is already used in some industrial treatment as part of a continuous treatment of effluent

Chapter 6

Studies on the Effects of Ultrasound

6. The Study of Ultrasound on the Reactions.

The use of ultrasound has been widespread throughout chemistry for many years [25, 26]. In an effort to see if any useful effect could be made on the Neutramag reactions, two visits were made to the Sonochemistry Division of the School of Environmental Sciences at the University of Coventry.

6.1 Introduction.

The use of high powered ultrasound has proved beneficial in many areas of chemistry. It has been used to give larger crystals, aid catalysis, initiate polymerisation reactions and affect reaction pathways in electro-chemistry as just a few examples [26, 27]. It has also been used in the treatment of industrial effluents and in assisting phase transfers, two areas of great importance to this project.

Ultrasound is defined as sound of a frequency above which the human ear cannot respond. The normal range of hearing is between 16Hz and 16kHz. Ultrasound is generally considered to be between 20kHz and 500kHz. There are three different types of ultrasonic tranducers,

gas driven - a high pressure flow of gas is converted to ultrasound,
    e.g. a dog whistle;
liquid driven - liquid is forced across a vibrating blade and so sonicated,
    e.g. cavitation from a ship's propeller;
electromechanical - conversion of electricity into sound. An application of the
    piezoelectric effect.

Most modern ultrasound uses the liquid or electromechanical induction methods. The piezoelectric effect is found in some crystals, where sudden compressions can cause a potential difference across opposite faces to occur. This property is also reversible, a contraction occurring on the application of a current. If a rapidly alternating current is applied, the contractions and expansions will cause vibrational energy.

Ultrasound enhances the reactivity of reactions in liquid media by generating and destroying cavitation bubbles. [28] Like normal sound waves, ultrasound is caused by a series of compression and rarefaction (stretching) waves, which pass through the medium. The bubbles are formed in the rarefaction wave when a sufficiently negative pressure is achieved, i.e. when the energy being put in becomes stronger than the attractive forces in the liquid structure. Following compression cycles, not necessarily the next ones as some cavitation bubbles can be stable over relatively long time scales (0.01s - 0.1s), cause these microbubbles to collapse, releasing a large amount of energy almost immediately. This release of energy causes localised "hot-spots" to occur, with temperatures in excess of 5000°c and pressures greater than 1000atm. Not only do these collapses cause these high pressure and temperature regions, but shockwaves are also produced which create enormous shear forces.

The vapours present in these microbubbles are affected by the sudden physical changes and are often fragmented, leaving reactive species such as radicals or carbenes. In an aqueous solution, the water is often broken up into $H^\bullet$ and $OH^\bullet$ radicals, which in turn can recombine or go on to form reactive species such as H_2O_2, **Figure 6.1**. [29,30]

$$H_2O \longrightarrow H^\cdot + OH$$

$$H^\cdot + O_2 \longrightarrow HO^\cdot_2$$

$$HO^\cdot_2 + HO^\cdot_2 \longrightarrow H_2O_2 + O_2$$

$$HO^\cdot + {}^\cdot OH \longrightarrow H_2O_2$$

Figure 6.1 Ultrasound Induced Radical Reactions of Water

The presence of these conditions and species will often allow reactions to occur that would be unavailable at lower energies.

The main effects of ultrasound that could benefit this project were the generation of physical forces and improved precipitation. [31] The shear forces present aid in the fragmentation of solid particles in the liquid. This should help the dissolution of the solid Neutramag particles. It should also benefit the reactions that utilise solids as co-reactants, e.g. $Fe^{(II)}/PPh_3$, $Fe^{(III)}/Al^{(III)}$ solutions and oxides, by breaking down the larger aggregates and so increasing the reactive surface areas.

Ultrasound has been used as a very effective method in aiding the precipitation of solids from solutions. [32] It produces very fine particles which act as seeds for the precipitation. As the precipitates grow, they are broken up, causing further seeds to form which enhances the precipitation process.

There will also be benefits to the reactions from the increased energy of the systems and improved mixing of the reactants.

The ultrasound experiments were undertaken to answer several questions

- was there any benefit to be gained by using ultrasound?
- was any of the effect attained not attributable to bulk energisation?
- was there any improvement in the reactions with solid additives?

6.2 Equipment.

The reactions were carried out in a 400ml beaker using 200ml of an approximately 1000ppm M^{2+} solution. The beaker was kept in a bowl of water in an attempt to help keep the temperature constant. This meant that any differences would be due to the effects of the ultrasound, rather than a general heating of the bulk solution. A smaller volume for these reactions, as compared to normal, was used to improve the efficiency of the sonication devices.

The ultrasound used in these experiments was produced by a Sonic and Materials Inc. 16kHz V1A probe with a Vibracell generator at a power setting of 5, and a 20kHz sonic bath at a power setting of 5. The probe, although at lower power, is more efficient than the bath as it interacts directly with the solution. The ultrasound from the bath must penetrate the glass of the container, reducing its efficiency. Also, regular pulses of ultrasound were tried. This was attempted to try to get a seeding effect in the solution, increasing reactivity and ease of dissolution, thus allowing the solid to precipitate better before the next burst was applied.

6.3.2 Temperature Analysis

20ml of 10,000ppm Ni^{2+} solution (3.41×10^{-3}mol) were taken and diluted to a volume of 200ml with distilled water. This gave an initial Ni^{2+} concentration of 1000ppm, (1.70×10^{-2}M). 1.43ml of the Neutramag slurry (3.76×10^{-3}mol) were added, giving a 10% excess for full stoichiometric reaction. The vessel was kept in a water bath to try to keep the temperature constant. The temperature of the reaction mixture was monitored using a digital thermometer and thermocouple and is shown in **Table 6.2**. The reaction was sonicated by the ultrasonic probe. A sample of the reaction mixture, approximately 80ml, was taken after 30 minutes and filtered to stop further reaction. The sonication was removed after 60 minutes and the water bath replaced with cold water. The reaction was left for a further 15 minutes before filtration. The concentration of nickel remaining in the filtrates was determined by atomic absorption. The results are shown in **Table 6.3**.

Table 6.2

Time /min	0	1	2	3	4	5	6
Temp /°C	23.2	25.2	26.9	28.6	30.3	31.2	32.3

Time /min	8	10	15	20	25	30	35
Temp /°C	34.2	36.1	39.5	42.4	45.3	47.5	49.5

Time /min	40	45	50	55	60	70	75
Temp /°C	51.3	52.5	53.6	54.6	55.6	35.5	32.7

Table 6.3

Time /min	Nickel Concentration /ppm
30	832
75	771

6.3.2.1 Thermal Control

20ml of 10,000ppm Ni^{2+} solution (3.41×10^{-3}mol) were taken and diluted to a volume of 200ml with distilled water. This gave an initial Ni^{2+} concentration of 1000ppm, (1.70×10^{-2}M). 1.43ml of the Neutramag slurry (3.80×10^{-3}mol) were added, giving a 10% excess for full stoichiometric reaction. The temperature of the reaction mixture was altered by the use of a water bath with a thermostat. The rate of heating was adjusted to achieve the desired temperatures at 10 minute intervals. A sample of the reaction mixture, approximately 80ml, was taken after 30 minutes and filtered to stop further reaction. The reaction was removed from the water bath after 60 minutes and allowed to cool for a further 15 minutes before filtration. The concentration of nickel remaining in the filtrates was determined by atomic absorption. The results are shown in **Table 6.4**.

Table 6.4

Time /min	pH	Nickel Concentration /ppm
30	7.96	880
75	8.21	870

6.3.3 Presonication of Neutramag

20ml of 10,000ppm Ni^{2+} solution (3.41×10^{-3}mol) were taken and diluted to a volume of 200ml with distilled water. This gave an initial Ni^{2+} concentration of 1000ppm, (1.70×10^{-2}M). 1.43ml of the Neutramag slurry (3.80×10^{-3}mol) were taken and diluted to a volume of 40ml. This diluted slurry was then sonicated for 5 minutes, before being added to the nickel solution, giving a 10% excess for full stoichiometric reaction. A sample of the reaction mixture, approximately 80ml, was taken after 30 minutes and filtered to stop further reaction. The reaction was stopped by filtration after 60 minutes. The concentration of nickel remaining in the filtrates was determined by atomic absorption. The results are shown in **Table 6.5**.

Table 6.5

Time /min	pH	Nickel Concentration /ppm
30	8.08	694
75	8.03	677

6.3.4 Reactions with Mixed Metals.

6.3.4.1 Reaction of Nickel$^{(II)}$ and Aluminium$^{(III)}$.

20ml of 10,000ppm Ni^{2+} solution (3.41×10^{-3}mol) and 20ml of 10,000ppm Al^{3+} solution (7.41×10^{-3}mol) were taken and diluted to a volume of 200ml with distilled water. This gave initial concentrations equivalent to 1000ppm for each metal, (1.70×10^{-2}mol Ni^{2+}; 3.71×10^{-2}mol Al^{3+}). 5.7ml of Neutramag slurry (1.49×10^{-2}mol) were added, giving a 10% excess for complete stoichiometric reaction. The ultrasound was applied, using the 16kHz probe, for 5 minutes, then the pH probe was introduced to the reaction mixture for 5 minutes before the pH was recorded. The pH probe was then removed and the ultrasound applied again. A sample of the reaction mixture was taken after 30 minutes and filtered to stop any further reaction. The reaction was stopped by filtration after 60 minutes. The concentrations of nickel and aluminium remaining in the filtrates were determined by atomic absorption. The results are shown in **Table 6.6**.

Table 6.6

Time /min	**pH**	**Nickel Concentration /ppm**	**Aluminium Concentration /ppm**
30	5.70	4.7	0.91
60	5.90	0.27	0.27

6.3.4.2 Reaction of Nickel$^{(II)}$ and Iron$^{(III)}$.

20ml of 10,000ppm Ni^{2+} solution (3.41×10^{-3}mol) and 20ml of 10,000ppm Fe^{3+} solution (3.58×10^{-3}mol) were taken and diluted to a volume of 200ml with distilled water. This gave initial concentrations equivalent to 1000ppm for each metal, (1.70×10^{-2}mol Ni^{2+}; 1.79×10^{-2}mol Fe^{3+}). 3.5ml of Neutramag slurry (9.13×10^{-3}mol) were added, giving a 10% excess for nickel for complete stoichiometric reaction. The ultrasound was applied, using the 16kHz probe, for 5 minutes, then the pH probe was introduced to the reaction mixture for 5 minutes before the pH was recorded. The pH probe was then removed and the ultrasound applied again. A sample of the reaction mixture was taken after 30 minutes and filtered to stop any further reaction. The reaction was stopped by filtration after 60 minutes. The concentrations of nickel and iron remaining in the filtrates were determined by atomic absorption. The results are shown in **Table 6.7**.

Table 6.7

Time /min	**pH**	**Nickel Concentration /ppm**	**Iron Concentration /ppm**
30	7.38	211	0.00
60	7.38	110	0.22

6.3.4.3 Reaction of Nickel$^{(II)}$ and Iron$^{(III)}$ Oxide.

20ml of 10,000ppm Ni^{2+} solution (3.41×10^{-3}mol) were taken and diluted to a volume of 200ml with distilled water. This gave an initial Ni^{2+} concentration of 1000ppm, (1.70×10^{-2}mol). 3.54g of ground iron(III) oxide were added. This was equivalent to 2.22×10^{-2} moles of "Fe_2O_3". 1.4ml of Neutramag slurry (3.76×10^{-3}mol) were added, giving a 10% excess for complete stoichiometric reaction. The ultrasound was applied, using the 16kHz probe, for 5 minutes then the pH probe was introduced to the reaction mixture for 5 minutes, before the pH was recorded. The pH probe was then removed and the ultrasound applied again. A sample of the reaction mixture was taken after 30 minutes and filtered to stop any further reaction. The reaction was stopped by filtration after 60 minutes. The concentrations of nickel and iron remaining in the filtrates were determined by atomic absorption. The results are shown in **Table 6.8**.

Table 6.8

Time /min	pH	Nickel Concentration /ppm	Iron Concentration /ppm
30	7.16	94	0.00
60	7.58	3.76	0.00

6.3.5 Reactions of Iron$^{(II)}$ and PPh$_3$.

6.3.5.1 Ultrasound.

Fresh solutions of iron$^{(II)}$ were prepared for each reaction.

9.95g of Fe(SO$_4$).7H$_2$O (3.58x10^{-2}mol) were dissolved to a volume of 200ml with distilled water, This gave a concentration of approximately 10,000ppm Fe^{2+} (1.79x10^{-1}M). 100ml of this solution were taken and diluted to a volume of 200ml with distilled water. This gave an initial Fe^{2+} concentration of approximately 5000ppm, (~8.95x10^{-2}M). To these solutions approximately 0.01g of well ground triphenylphosphine (PPh$_3$) was added and the pH recorded. This gave a molar ratio of approximately 250:1 Fe^{2+}:PPh$_3$. 7.5ml of Neutramag slurry (1.97x10^{-2}mol) were added, giving a 10% excess for complete stoichiometric reaction. The ultrasound was applied, using the 16kHz probe, for 5 minutes, then the pH probe was introduced to the reaction mixture for 5 minutes before the pH was recorded. The pH probe was then removed and the ultrasound applied again. A sample of the reaction mixture was taken after 30 minutes and filtered to stop any further reaction. The reaction was stopped by filtration after 60 minutes. The concentration of iron remaining in the filtrates was determined by atomic absorption. The results are shown in **Table 6.9**.

Table 6.9

Time /min	pH	Iron Concentration /ppm	% Iron removed
30	6.47	3722	25
60	6.71	2490	50

6.3.5.2 Presonication of the PPh_3 Suspension.

9.95g of $Fe(SO_4).7H_20$ (3.58×10^{-2}mol) were dissolved to a volume of 200ml with distilled water, This gave a concentration of approximately 10,000ppm Fe^{2+} (1.79×10^{-1}M). 100ml of this solution were taken and diluted to a volume of 200ml with distilled water. This gave an initial Fe^{2+} concentration of approximately 5000ppm, (~8.95×10^{-2}M). To these solutions approximately 0.01g of well ground triphenylphosphine (PPh_3) was added and the pH recorded. This gave a molar ratio of approximately 250:1 Fe^{2+}:PPh_3. The ultrasound was applied to the Fe/PPh_3 suspension, using the 16kHz probe, for 5 minutes, then the pH probe was introduced to the reaction mixture. 7.5ml of Neutramag slurry (1.97×10^{-2}mol) were added, giving a 10% excess for complete stoichiometric reaction A sample of the reaction mixture was taken after 30 minutes and filtered to stop any further reaction. The reaction was stopped by filtration after 60 minutes. The concentration of iron remaining in the filtrates was determined by atomic absorption. The results are shown in **Table 6.10**.

Table 6.10

Time /min	pH	Iron Concentration /ppm	% Iron removed
30	7.44	4218	15
60	7.55	3444	31

6.3.5.3 Control Reaction

9.95g of $Fe(SO_4).7H_20$ (3.58×10^{-2}mol) were dissolved to a volume of 200ml with distilled water, This gave a concentration of approximately 10,000ppm Fe^{2+} (1.79×10^{-1}M). 100ml of this solution were taken and diluted to a volume of 200ml with distilled water. This gave an initial Fe^{2+} concentration of approximately 5000ppm (~8.95×10^{-2}M). To these solutions approximately 0.01g of well ground triphenylphosphine (PPh_3) was added and the pH recorded. This gave a molar ratio of approximately 250:1 Fe^{2+}:PPh_3. 8.0ml of Neutramag slurry (1.97×10^{-2}mol) were added, giving a 10% excess for complete stoichiometric reaction A sample of the reaction mixture was taken after 30 minutes, and filtered to stop any further reaction. The reaction was stopped by filtration after 60 minutes. The concentration of iron remaining in the filtrates was determined by atomic absorption. The results are shown in **Table 6.11**.

Table 6.11

Time /min	pH	Iron Concentration /ppm	% Iron removed
30	8.25	3660	32
60	8.30	3300	34

6.4 Discussion

6.4.1 Preliminary Reactions.

These reactions were undertaken to ascertain if there was any benefit to be obtained by using ultrasound with Neutramag. It wasn't known at the time if there would be discernible effect on the reactions, so only basic information was acquired.

The first metal ion to be tested was Cu^{2+}. Although there was not much room for substantial improvement, as copper already worked well on its own, it was hoped that an increase in the rate of the reaction would be observed. A control reaction using no ultrasound was run in the same conditions first. The reactions using ultrasound were not run for as long as the control, but it was hoped that there would have been an increase in the overall rate to achieve completion. It would have been helpful to run these reactions completely, but there were time limits to their study.

The reactions progress were followed by observing their pHs, the levelling off of the pH indicating that the reaction had gone to completion. This was, on reflection, an incorrect assumption.

6.4.1.1 No Ultrasound.

As expected the control reaction went to completion after about an hour, **Figure 6.2**, with all of the metal removed from the solution. The pH profile of the reaction is shown in **Table 6.2**.

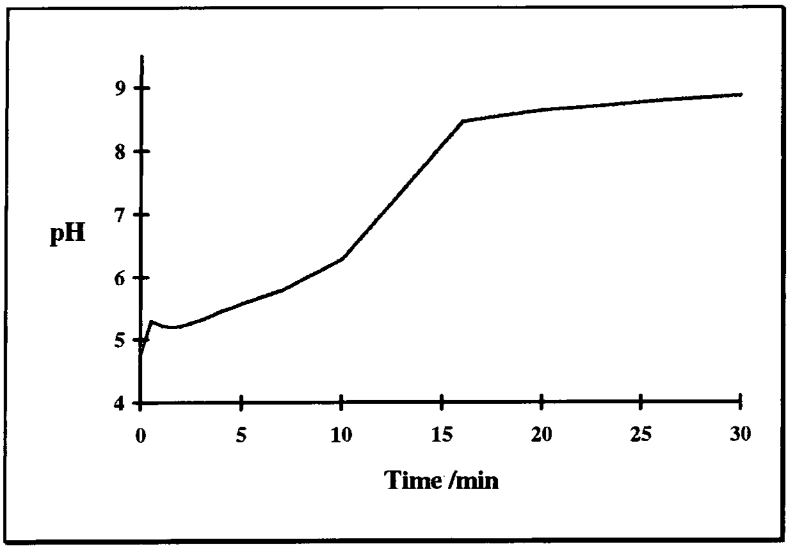

Figure 6.2 pH of Cu^{2+} Reaction with Neutramag and No Ultrasound

Note that only the data for the first 30 minutes are shown in the graph, to give an easy comparison with the ultrasound reactions.

6.4.1.2 Ultrasonic Probe.

The reaction with the 16kHz probe achieved the same final pH after only approximately half the time, although there was 3ppm of Cu^{2+} remaining in solution at that time, **Figure 6.3**. It seems likely that, although the pH values were approximately the same, there was still some reaction occurring.

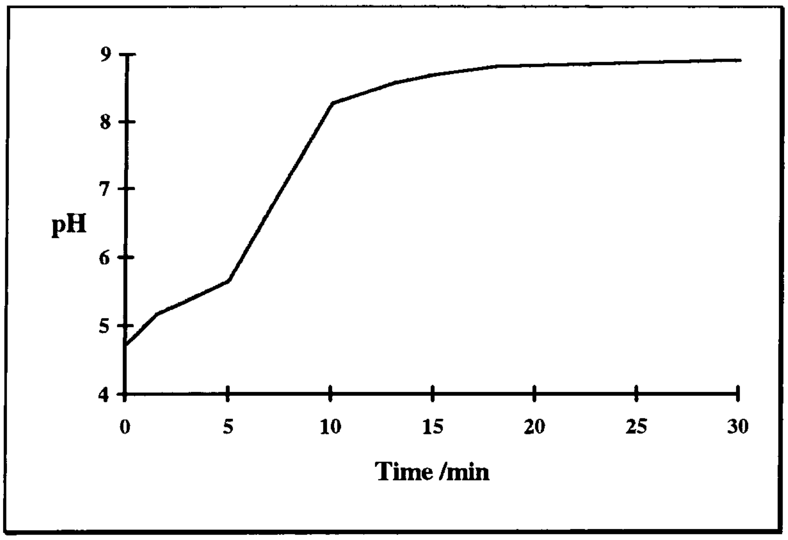

Figure 6.3 pH of Cu^{2+} Reaction with Neutramag and Ultrasonic Probe

6.4.1.3 Pulsed Ultrasonic Probe.

The reaction was repeated using the pulse option, 1 second on - 1 second off. The results were much as hoped for. The increase in the rate of the first part of the reaction was still present and slightly sharper, even though the ultrasound had been applied over only the half the time, **Figure 6.4**

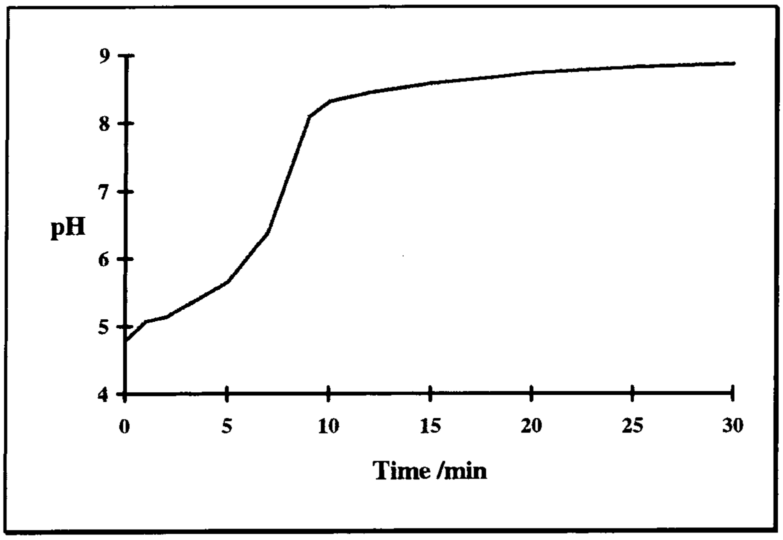

Figure 6.4 pH of Cu^{2+} Reaction with Neutramag and Pulsed Ultrasonic Probe

6.4.1.4 Ultrasonic Bath.

Finally the sonic bath was tried. This was done without the usual stirring of the solution. The pH still rose to roughly the same value and gave a final concentration of less than 5ppm. Although, as expected, the increase was not so pronounced, there was an improvement even without the solution being stirred, **Figure 6.5**.

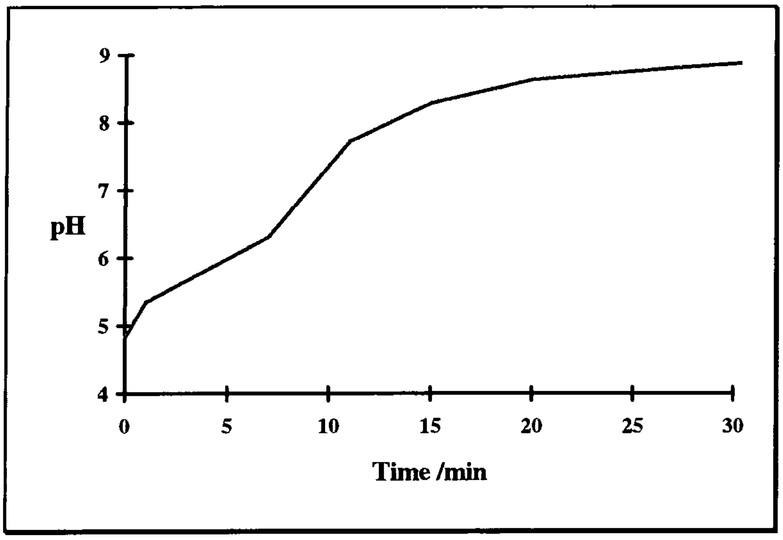

Figure 6.5 pH of Cu^{2+} Reaction with Neutramag and Ultrasonic Bath

As the reactions took place it was found that the ultrasound affected the pH probe that was being used to monitor the reactions. The best way to overcome this problem was to apply the ultrasound for some length of time, turn it off, then take a pH reading once the reading had settled. This was, in effect, a long term pulsing of ultrasound.

6.4.1.5 Iron(II) Reactions.

Iron(II) was the next metal ion to be tried. Accurate final concentrations were unable to be obtained as the atomic absorption spectrometer would not calibrate very well.

Although the actual amounts removed were difficult to determine, one fact was discovered. As the solutions were filtered at the end of the reaction, the residue was seen to be very brown. This meant that there had been substantial oxidation of the iron, without any excess aeration. This was probably due to the ultrasound. The sonics also affect the water in the solution, forming HO$^\bullet$ radicals and also H_2O_2, a strong oxidising agent, **Scheme 6.1**. The peroxide would aid the oxidation of the iron(II) solutions.

$$2[Fe(H_2O)_6]^{2+} + H_2O_2 + 2H^+ \longrightarrow 2[Fe(H_2O)_6]^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + HO^\bullet + H^+ \longrightarrow [Fe(H_2O)_6]^{3+} + H_2O$$

Scheme 6.1

6.4.2 Thermal Analysis.

As the ultrasound was applied to the reactions there was some noticeable increase in the temperature. Although this is only a small part of the energy being added to the systems, it could have a large effect on the outcome of the amount precipitated. Increasing the temperature would aid the dissolution of the Neutramag and increase the rate of reaction.

To look at this effect a reaction was sonicated and the temperature monitored with a digital thermometer. A reaction was also run without ultrasound, increasing the temperature at the same rate using a thermostat.

The ultrasound raised the temperature of the reaction up to approximately 55°C after an hour, even with the cooling bath. The % metal ion removed was improved in this reaction by 15%. The thermal reaction also gave an improved removal, but only of the order of 5%. This indicates an improvement of 10% in the reaction due to the effects of the ultrasound rather than the heating of the bulk suspension. The precipitation of nickel(II) from solution is not an easy reaction, and a 10% improvement is not insignificant. This reaction was not repeated due to time constraints, and although there was no accurate reproducibility, this indicated an effect other than simple heating.

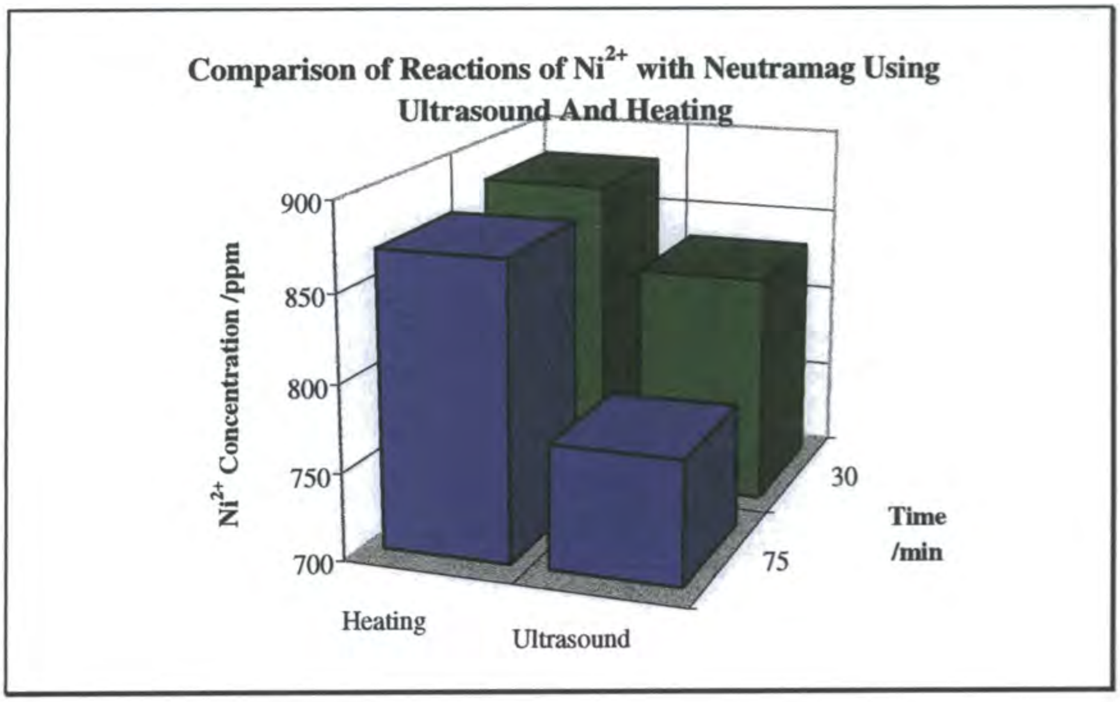

Figure 6.6

6.4.3 Presonication of Neutramag.

The effect of ultrasound on solids is well known [33]. The extreme physical forces present when the cavitation bubbles collapse cause fragmentation of the particles. In the case of the sonication of the Neutramag slurry this would be an aid to the dissolution of the solid. This process is vital for the reactions to continue to completion.

The results shown in **Figure 6.7** indicate a much larger removal of Ni^{2+} from the solution than would be expected. There is an improvement of approximately 25% after 75 minutes, compared with the levels reached without sonication. This is a large increase in removal for the amount of energy added, only requiring ultrasound prior to the treatment of the effluent.

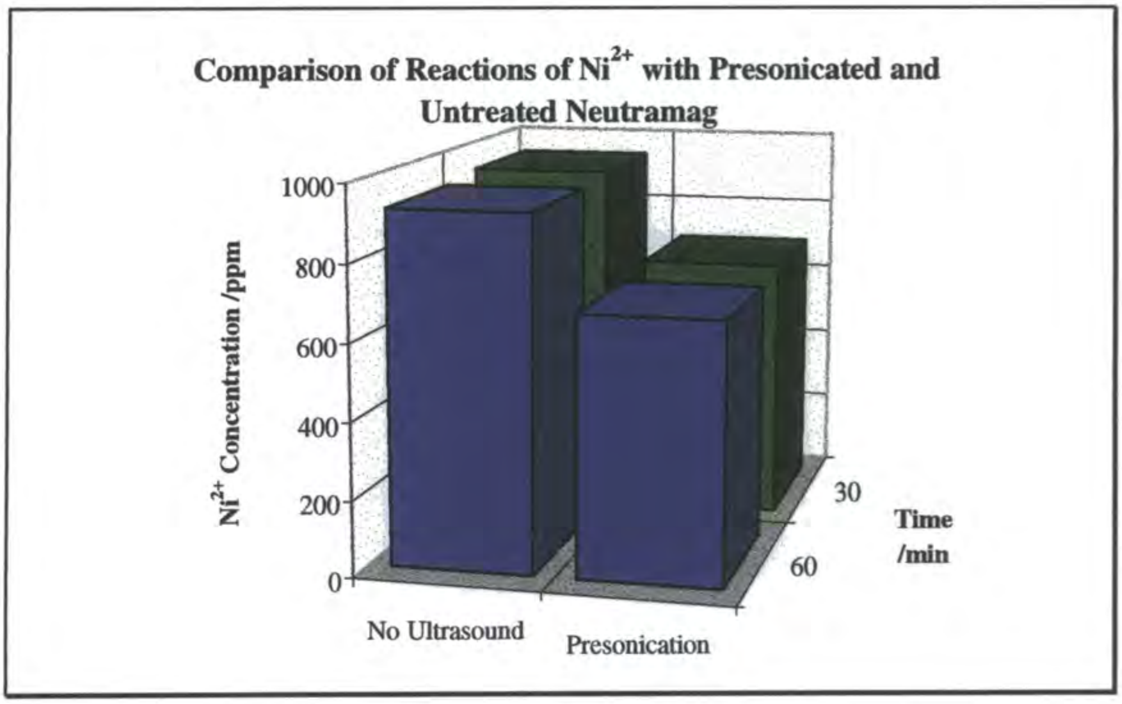

Figure 6.7

The smaller particle size of the Neutramag solids in the slurry achieved by the ultrasound would require a greater amount of precipitated $Ni(OH)_2$ to coat the undissolved $Mg(OH)_2$, which is believed to prevent the reactions from proceeding to completion.

The Neutramag slurry was noticeably warm to the touch through the beaker, before addition to the metal solution, after sonication. This increased temperature may account for some of the increase in metal ion removal although the average temperature of the reaction mixture would not be greatly affected due to the larger volume of metal ion solution which had not been heated.

6.4.4 Mixed Metal Reactions.

The fragmentation effect of ultrasound on solid particles would also benefit the reactions which have had solids added, by increasing the surface area and hence the reactivity. These reactions include the additions of $M^{(III)}$ solutions and solid oxides.

Some of the additives in these reactions were added as solutions (of Al^{3+} or Fe^{3+} salts). These were precipitated at a much lower pH, approximately pH 4-5, and as such were present as solids by the time the precipitation of $Ni(OH)_2$ started to occur, at approximately pH 7-8.

The ultrasound would have the same beneficial effects on the reaction as with the standard reactions of Ni^{2+} with Neutramag, i.e. increased solubility of the Neutramag and increased temperature, but would also have an effect on the $M^{(III)}$ solids. The breakdown of the solid aggregates would increase their reactive surface areas, and increase the amount of precipitated $Ni(OH)_2$ needed before coating of the Neutramag particles occurred and prevented the reactions from continuing.

6.4.4.1 Nickel and $Al^{(III)}$ Solution.

The reactions of nickel with aluminium solution present had been shown to have a large increase in reactivity, **Chapter 4**. Final concentrations of the order of 20ppm were achieved, far lower than for single metal reactions. Although these results were much better the metal concentrations were not low enough to allow discharge of similar effluents.

Treatment with ultrasound in these reactions further increases the metal ion concentration to below the discharge levels. This makes solutions with high Ni^{2+} content completely treatable with Neutramag, within the time constraints of industrial processes, for the first time.

Figure 6.8 shows a comparison of the levels achieved using the different reaction conditions. Each of the reactions had an initial concentration of 1000ppm and was treated with a 10% excess of Neutramag. The Al^{3+} solutions used were initially 1000ppm. Preventing the formation of larger particles with the ultrasound seemed to allow the reaction to proceed to completion.

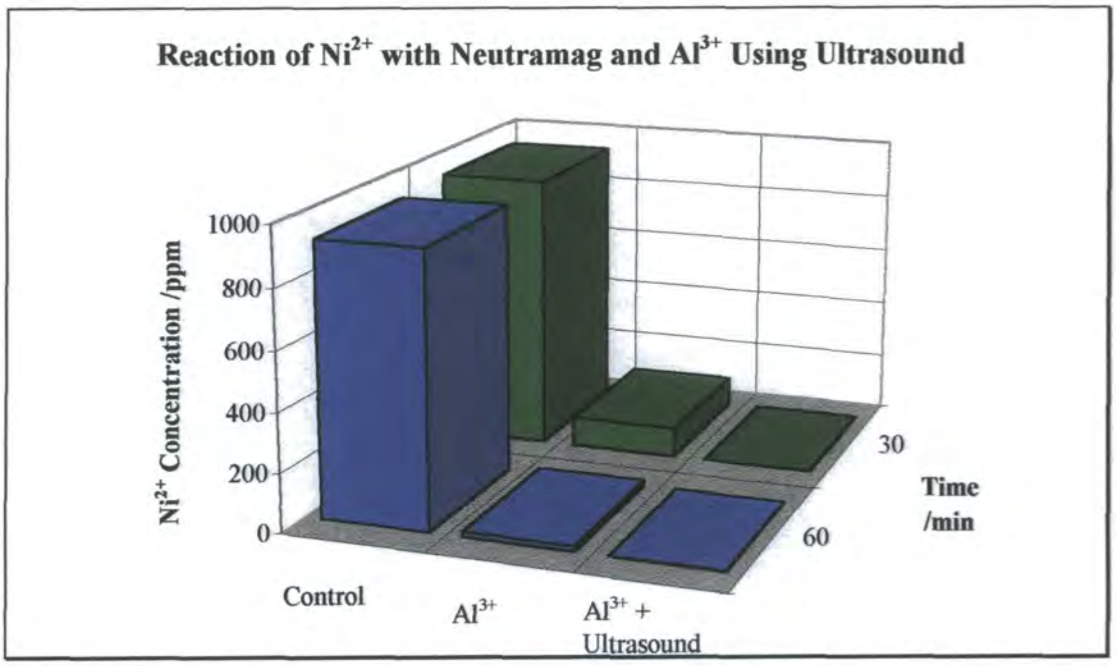

Figure 6.8

6.4.4.2 Nickel and Fe^{3+} Solution.

Reactions using iron(III) instead of aluminium had also been tried and were seen to have a similar effect, although to a lesser extent. The improvements in metal ion removed were still considerable, but nowhere near good enough. The sonication of these reactions further increased the metal ion removal, but again not to the same level as with aluminium solutions.

The solid oxide also had the benefits of not needing extra Neutramag to precipitate it and could be re-used in later reactions, acting as a pseudo-catalyst.

Figure 6.10 shows the comparison between the different reactions with Fe_2O_3. Each of the reactions had an initial concentration of 1000ppm and was treated with a 10% excess of Neutramag.

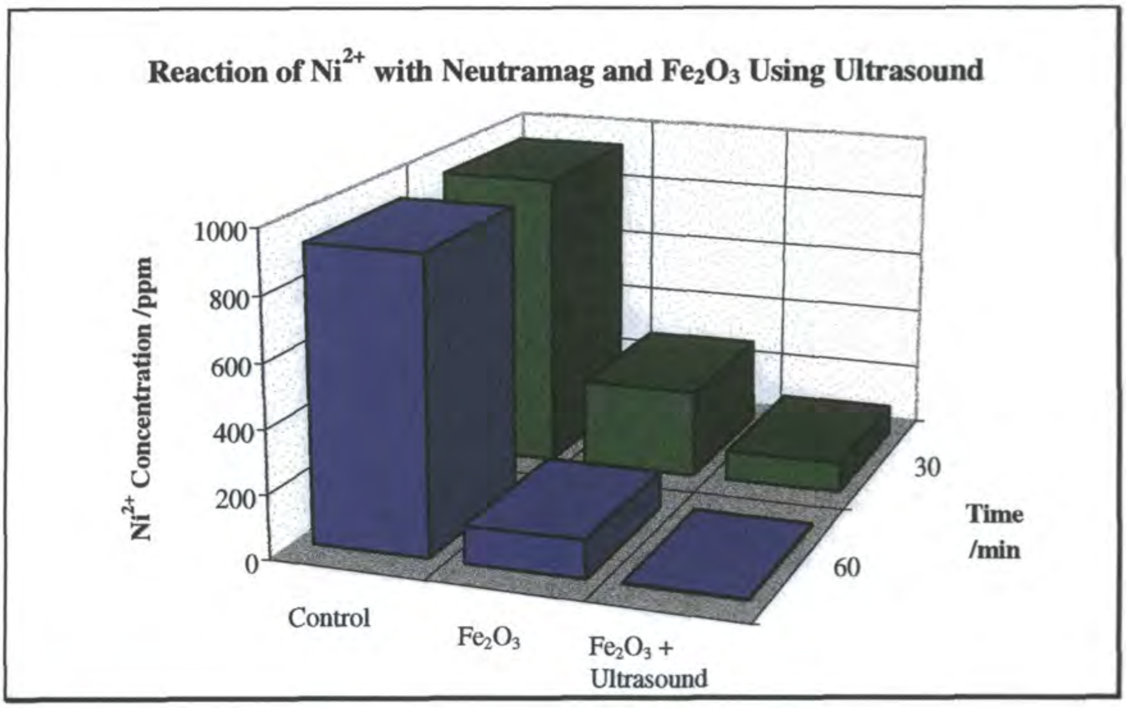

Figure 6.10

6.4.5 $Fe^{(II)}$ Reactions.

Triphenylphosphine (PPh_3) had been seen to have a greatly beneficial effect on reactions involving $Fe^{(II)}$. Addition of only small fractions of the amount of $Fe^{(II)}$ present have made large improvements in the % metal ion removal, **section 3.3.2**.

One of the difficulties in using PPh_3 is that it is highly insoluble in water, which limits its effectiveness in these aqueous reactions. The use of ultrasound in these reactions was to aid in the break-up of the larger PPh_3 particles and increase their reactive surface areas.

In the preliminary reactions $Fe^{(II)}$ was reacted with Neutramag in the presence of ultrasound. Although no analysis to determine the final Fe concentration was possible at that time, one fact was noticed.

Fe^{2+} ordinarily precipitates as a light green solid, FeO, but when the reaction is performed with sonication of the mixture, the dark brown solid of Fe^{3+}, in the form of Fe_2O_3, is found. The colour change is quite pronounced and is spread uniformly throughout the solid formed. This was not totally unexpected, as one of the properties of ultrasound is to affect the bulk medium of the reaction, in this case water, forming reactive species such as radicals, **Figure 6.1**. The formation of these radical species and the formation of peroxides from them would easily cause the oxidation of $Fe^{(II)}$.

$$2Fe^{2+} + H_2O_2 + 2H^+ \longrightarrow 2Fe^{3+} + 2H_2O$$

Equation 6.1

The reactions in ultrasound which had the ligand present show no signs of this oxidation, the light green colour of $Fe^{(II)}$ being found throughout the solids. This seemed strange as the effect was achieved for the entire sample while only a fraction of the amount of ligand had been added.

It as already been mentioned that PPh_3 interacts with Fe^{2+} in these reactions, rapidly bonding and separating again. This could lead to interference with the oxidation process of the peroxides and radicals formed in the sonication of the aqueous medium.

Another possibility is that the ligand hinders the production of the oxidising species, $HO^{\bullet}/H_2O_2$, in the reactions and thus prevent the interaction with the metal ions. This is possibly done by absorbing the initial energy transfer.

These observations were derived from the colour of the precipitating hydroxides. For a more accurate determination of the amounts of Fe(II) and Fe(III) present in the precipitates tests must be used, simple titrations with dichromate will perform this test adequately.

6.5 Conclusions.

These studies have shown several results with the use of ultrasound on Neutramag reactions.

- an increase in metal ion removal and rate is seen
- the increase is greater than that observed by simply heating the system to the same temperatures
- it further improves the reactivity of $M^{(III)}$ additive reactions, especially with the $M^{(III)}$ oxides
- donor ligand reactions are further improved
- PPh_3 stabilizes $Fe^{(II)}$ to oxidation

These results may indicate a minimum amount of metal ion removal for each system. The mixtures were filtered using Whatman No1 filter paper in a Buchner funnel. In some of the filtrates there seemed to be very small particles still present, as opposed to solutions. The fragmentation effect of the ultrasound may have affected the precipitates of the metals. If these precipitates had been broken down by the ultrasound, they may have passed through the filter paper and registered in the A.A. analysis, while still having been precipitated. Improving the method of filtration could thus increase the metal ion removal seen here still further. Settling or fine filter beds may decrease the final concentration of metals in solution. Using ultrasound in an early part of the treatment, then adding coagulants, may be a possible solution for these cases.

There is a possible drawback with the use of ultrasound with Neutramag. Producing smaller particles negates one of the main benefits of using Neutramag in these processes, that of smaller residual sludge volumes. The smaller particles will retain water more effectively and therefore possess more volume and mass when upon its disposal.

Industrially, the process must be looked at in terms of costs. The use of ultrasound will improve most reactions encountered in effluent treatment, but it is more expensive. The equipment must be purchased, installed and maintained, and the system needs to be powered whenever in use. These costs must be balanced against the costs of buying and using higher excesses of reagents, such as Neutramag, to increase the metal ion removal to the same levels. A cost comparison of the two methods is, however, far beyond the scope of this project.

Chapter 7

Conclusions

7. Conclusions.

7.1 Summary of this Project.

Reactions performed with single metal systems using donor ligands failed to show the improvements hoped for with most metal ions.

- Fe^{2+} showed similar benefits to those seen in the previous project.
- Cu^{2+} solutions were actually affected detrimentally, less metal ion being removed with the addition of ligands.
- Ni^{2+} also showed some small decreases in % removed with the addition of ligands. These decreases were less easy to see than those with Cu^{2+} as the removals were much poorer.
- Zn^{2+} and Pb^{2+} showed little effect with the addition of ligands.
- Al^{3+}, which was expected to be very simple to precipitate, showed a surprising difficulty in treatment. The presence of SO_4^{2-} ions in the reaction mixture completely removed this problem. This may indicate that anions present in the solution can affect the way in which a reaction proceeds, and may need to be taken into consideration when analysing an effluent.

The lack of effect with these metal ions could be due to several factors. The Irving-Williams Series, **Figure 1.3**, indicates that the metals forming more stable complexes could bond permanently with the ligand species, which would remove the additive from any further reaction and create a small percentage of soluble complex which could not be precipitated.

Formation constants for Fe^{2+}-L complexes seem to be such that the ligands can interact, but not strongly enough to bind permanently, and so can be readily displaced by OH^- ions. This hypothesis was described in **section 1.4** and **Scheme 1.1**.

In the case of Ni^{2+} the reactions are stopped completely after approximately minutes, and leaving them for longer time periods does not increase the metal ion removal. In the effluents studied in the previous project, good metal ion removals were obtained in these mixed metal systems and so the addition of other metals to Ni^{2+} and Zn^{2+} systems were studied in particular.

This new subject ignored the addition of catalytic quantities of ligands and concentrated on adding stoichiometric quantities of metal ions. Using Fe(II) improved the amount of Ni^{2+} precipitated, but reduced the amount of Fe^{2+} removed. Exchanging Fe(II) for Fe(III), which is very easy to precipitate, gave a large increase in the Ni^{2+} removal and complete removal of the Fe^{3+}. Adding Al^{3+} showed even better results although decreasing the amount of Al^{3+} added decreased the metal ion removals. Using the easily precipitated M(II) ion Cu^{2+} gave comparatively small improvements. Testing the effect of these additions on the precipitation of Zn^{2+} instead of Ni^{2+} showed greater improvements for M(III), Al^{3+} again giving higher metal ion removal than Fe^{3+}. Zn^{2+} gave far better results with Cu^{2+}, although stoichiometric amounts were still required. Testing Fe^{2+} with Al^{3+} also gave greatly improved removals.

A commercially available reagent, Ferral, consisting of similar components to those used previously and marketed for this process, was obtained and tested with Ni^{2+} and Zn^{2+} solutions. The metal ion removals steadily increased with increasing reaction time and increased addition of Ferral. The addition of these M(III) species means that more Neutramag is required to treat the solution. The additions were seen to be more effective than adding the same amounts of Neutramag without the Ferral. Increasing the amount of Ferral added improved the metal ion removal more in the earlier parts of the reactions; hence conditions could be tailored to favour either a faster rate of reaction or the use of smaller quantities of M(III)s and Neutramag if time is not a constraint.

The greatest final improvement was not seen with the largest addition, however, as the metal ion removal of the solution treated with the corresponding higher excess of Neutramag increased, whereas the Ferral reaction did not increase the removal as much, since it was already virtually completed. The highest improvement was obtained with the addition of 5-10ml of Ferral to 1000ppm solutions of Ni^{2+} or Zn^{2+}.

Zn^{2+} showed better metal ion removals than Ni^{2+} with these reactions, although the reactions with high excesses of Neutramag also improved.

Most of the single metal reactions seemed to show a point at which no further reaction was seen. If the reactions had just stopped and the equilibria were not sufficient to produce any further precipitation, then the Neutramag itself should dissolve to its buffer concentration at approximately pH 10.5. As this does not occur, reaction pHs remaining between 7 and 8.2 for most metal ions, another factor must be present.

The solid Neutramag particles are hydrated MgO, which have a region of concentrated $Mg(OH)_2$ surrounding them where the pH is relatively high [35]. This region would be ideal for reaction with M(II) species. Due to the close proximity of the solids being formed, the Neutramag solids could act as seeding sites for M(II) precipitation. As more M(II) is precipitated the solid Neutramag particles could become coated with the insoluble $M(OH)_2$ and effectively removed from the reaction mixture. This would prevent further dissolution of $Mg(OH)_2$, and greatly reduce the possible amount of precipitation. Coating of MgO particles by $Ni(OH)_2$ is known [23] and so this seems a reasonable theory. **Figure 7.1** shows a scanning electron micrograph of these nickel coated magnesia particles. The white bar at the side of the image represents 1000μm.

Figure 7.1 Scanning Electron Micrograph of $Ni(OH)_2$ Coated Magnesia Particles

The addition of other metal species into the reaction seems to hinder this process, so that it did not occur. There seems to be a preference for interacting with the M(III) hydroxides rather than the $Mg(OH)_2$ particles, which lets the reactions proceed further. The results show a preferential order in which the hydroxides interact with one another shown in **Figure 7.2**.

Zn-Al > Zn-Cu > Ni-Al > Zn-$Fe^{(III)}$ > Ni-$Fe^{(III)}$ >> Ni-Cu > Ni-Mg > Zn-Mg > Ni-Ni > Zn-Zn

Figure 7.2 Order of Increasing Interactions Between Metal Hydroxides

If there is no other metal present to interact with Ni^{2+} or Zn^{2+}, then the precipitating M(II) will interact with $Mg(OH)_2$ rather than another M(II) species. This unwillingness to interact with itself requires the addition of stoichiometric amounts of the M(III) additives, as they, too, are ineffective at lower concentrations.

This preferential interaction of an M(II) species with a pre-precipitated M(III) derivative rather than with $Mg(OH)_2$ is probably connected with variations in ionic radii, **Table 7.1**, and polarisability.

Table 7.1[36]

Metal ion	**Ionic radius /Å**
Al^{3+}	0.51
Cr^{3+}	0.63
Fe^{3+}	0.64
Mg^{2+}	0.66
Ti^{4+}	0.68
Ni^{2+}	0.69
Cu^{2+}	0.72
Fe^{2+}	0.74
Zn^{2+}	0.74
Pb^{2+}	1.20

The metal ions with the smallest ionic radii are also those that aid the reactions the most. Ions with radii smaller than that of Mg^{2+} aid precipitation and those with radii larger hinder it. Cu^{2+} is an anomaly here. The figure given here, 0.72Å, is larger than that of Mg^{2+}, but benefits are seen. This is due to the fact that the figure given in the table is an average radius, due to its distorted configuration because of the Jahn-Teller Effect. The more highly charged hydroxy- species would interact with the shorter "equatorial" positions rather than the "axial" ones and so the effective ionic radii would be smaller for these interactions.

Smaller radii, and higher charges, would increase the polarising power of the cation, creating stronger bonding with the hydroxo-, or oxo-,complexes and having a greater influence outside the primary coordination sphere. This could lead to greater attraction for other polar species, such as precipitating metal(II) hydroxides.

Each of these treatments required the addition of much more Neutramag along with the M(III) species. These species will already be present in solid form by the time the M(II) species start to precipitate, due to the comparative K_{SP}s of the hydroxides. As this is the case, an attempt was made to replace the M(III) solutions with M(III) solids, which had the benefit of not needing extra Neutramag to treat them. The species added were M(III) oxides, as these would be very similar to the products of the precipitated M(III) solutions. One idea was the re-use of residues from previous reactions. These residues would contain both metal oxides and Neutramag which was unreacted. Both of these components were expected to improve the reactions. A slight improvement was seen as more residue was added, but not as much as hoped. Other M(III) and M(IV) oxides, including Cr_2O_3 and TiO_2, were then tested, to observe any changes with increased charge. Ni^{2+} did show some gradual improvement with increasing addition of the oxides. These improvements were nowhere near the levels obtained using the solutions, even with far greater amounts added. The solid would be present in larger particles which would have less total surface area with which to interact with the precipitating metal(II) ions. This would greatly reduce their effectiveness, and could explain the lower metal ion removal obtained.

Introduction of energy into the reactions in the form of ultrasound proved to be an effective method of increasing metal ion removal. Not only were the final concentrations lower but the rates of reaction also improved. The benefits seen using ultrasound were shown to be greater than those seen with simple heating of the reactions, indicating that a separate effect was .

The physical properties of the ultrasound, the large shear forces etc., aided the reactions that utilised other solid particles in the precipitation of metal hydroxides, i.e. M(III) additions, both solution and solid oxide. The breakdown of the precipitating particles would increase the effective surface area, reducing the level of coating produced on both Neutramag particles and on M(III) solids which limit their effectiveness. It would also, however, limit the improved draining ability of Neutramag precipitated hydroxides. This point and the cost of installing and running the sonicating equipment would need to be balanced against the improvements in metal ion removal.

In general the project has been successful. The aim was to improve both amount of metal ion removal and understanding of the problems behind treatment of metal ions solutions with $Mg(OH)_2$. This has been accomplished with ligand addition showing limited use with many metal ions, the only systems which really benefited from them being those consisting mainly of Fe^{2+}. The addition of other metals to the treatments improved the removal of metal ions in all cases tested, which outweighed the use of much higher excesses of Neutramag.

7.2 Summary of Treatment Methods.

Table 7.2 shows a summary of the various treatment methods, their requirements and uses.

Table 7.2

Metal Ion	Method	Requirements	Comments
Al^{3+}	Neutramag	SO_4^{2-} required	poor removal obtained without the presence of SO_4^{2-}; can be used with other metal as a precipitation aid; no risk of redissolution at pH
Cu^{2+}	Neutramag	minimised concentrations of donor ligands	binding ligands caused proportional reduction in removal of Cu^{2+} ;limited benefit as a co-precipitant with other metal ions
Fe^{2+}	Neutramag + aeration	constant supply of air passed through the solution	oxidation of Fe^{2+} to Fe^{3+} provided an effective route for removal
	Neutramag + ultrasound	ultrasound equipment and power	increased energy of reaction, improved rate and removal; effect of ultrasound on H_2O provided oxidation of Fe^{2+} to Fe^{3+}
	Neutramag + donor ligands	catalytic quantities of donor ligands	complete removal of Fe^{2+} achieved with very small (≤1%) additions of donor species
Fe^{3+}	Neutramag		can be used with other metal ions as a precipitation aid
Ni^{2+}	Neutramag + heat	heating of solutions or suspensions	heating prevents cessation of reaction before completion
	Neutramag + M^{3+}	stoichiometric amounts of M^{3+} and extra Neutramag for it's precipitation	co-precipitation provides preferred formation sites freeing undissolved Neutramag
	Neutramag + ultrasound	ultrasound equipment and power	increased energy of reaction, improved rate and removal; can use in conjunction with M^{3+}
Pb^{2+}	Neutramag		use of donor ligands showed no effect
Zn^{2+}	Neutramag +M^{3+}	stoichiometric amounts of M^{3+} and extra Neutramag for it's precipitation	co-precipitation provides preferred formation sites freeing undissolved Neutramag
	Neutramag + ultrasound	ultrasound equipment and power	increased energy of reaction, improved rate and removal; can use in conjunction with M^{3+}

7.3 Future Work.

There are several aspects of this study which remain incomplete.

- Treatment of copper solutions which have high concentrations of donor species present has still to be improved. Reaction of the NH_3 with a cheap reagent can be looked at in further detail.

- Identification of the intermediate, probably $[Fe(H_2O)_5L]^{2+}$, in the iron/ligand reactions could be attempted. Use of infra-red and NMR (^1H and ^{31}P) techniques should be able to identify the complexed species. The low concentrations of the intermediates would hinder this work, however. A further problem with the use of NMR techniques with these systems woiuld be that many of the species are paramagnetic. Only diamagnetic metal ions such as Al^{3+}, Zn^{2+}, Pb^{2+} or low spin Fe^{2+}, a d^6 octahedral system, could be effectively observed from the species used in this work. As Al^{3+} is so easily precipitated, the use of ^{27}Al NMR is limited.

- Confirmation of coating in these reactions would back up the theories put forward in this work. Scanning electron microscopy and X-ray techniques could be used to observe Neutramag and M(III) solids being coated by the precipitated metal ions. Powder defraction could be used to study the residues from the filtrations.

- Further work with improved filter techniques could be useful. The use of surfactants or coagulants to improve aggregation of particles could be used towards improved filtration. These additions must balance effectiveness against cost. Separate Britmag projects have concentrated on this area.

Chapter 8

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Appendix A

Lists of Tables, Figures, Equations and Schemes

List of Tables.

List of Figures.

List of Equations.

List of Schemes.

Appendix B

List of Colloquia, Lectures and Seminars

Colloquia, Lectures and Seminars from Invited Speakers.

The following colloquia, lectures and seminars were attended.

1994 - 1995 (August 1 - July 31)

October 5 Prof. N. L. Owen, Brigham Young University, Utah, USA.
Determining Molecular Structure - the INADEQUATE NMR way

October 19 Prof. N. Bartlett, University of California
Some Aspects of Ag(II) and Ag(III) Chemistry

November 2 Dr P. G. Edwards, University of Wales, Cardiff
The Manipulation of Electronic and Structural Diversity in Metal Complexes - New Ligands

November 3 Prof. B. F. G. Johnson, Edinburgh University
Arene-metal Clusters

November 9 Dr G. Hogarth, University College, London
New Vistas in Metal-imido Chemistry

November 10 Dr M. Block, Zeneca Pharmaceuticals, Macclesfield
Large-scale Manufacture of ZD 1542, a Thromboxane Antagonist Synthase Inhibitor

February 1 Dr T. Cosgrove, Bristol University
Polymers do it at Interfaces

February 8 Dr D. O'Hare, Oxford University
Synthesis and Solid-state Properties of Poly-, Oligo- and Multidecker Metallocenes

February 22 Prof. E. Schaumann, University of Clausthal
Silicon- and Sulphur-mediated Ring-opening Reactions of Epoxide

March 1 Dr M. Rosseinsky, Oxford University
Fullerene Intercalation Chemistry

March 22 Dr M. Taylor, University of Auckland, New Zealand
Structural Methods in Main-group Chemistry

April 26 Dr M. Schroder, University of Edinburgh
Redox-active Macrocyclic Complexes : Rings, Stacks and Liquid Crystals

1995 - 1996 (August 1 - July 31)

October 13	Prof. R. Schmutzler, University of Braunschweig, FRG. Calixarene-Phosphorus Chemistry: A New Dimension inPhosphorus Chemistry
October 25	Dr.D.Martin Davies, University of Northumbria Chemical reactions in organised systems.
November 15	Dr Andrea Sella, UCL, London Chemistry of Lanthanides with Polypyrazoylborate Ligands
November 22	Prof. I Soutar, Lancaster University A Water of Glass? Luminescence Studies of Water-Soluble Polymers.
November 29	Prof. Dennis Tuck, University of Windsor, Ontario, Canada New Indium Coordination Chemistry
January 10	Dr Bill Henderson, Waikato University, NZ Electrospray Mass Spectrometry - a new sporting technique
January 17	Prof. J. W. Emsley , Southampton University Liquid Crystals: More than Meets the Eye
January 24	Dr Alan Armstrong, Nottingham Univesity Alkene Oxidation and Natural Product Synthesis
February 12	Dr Paul Pringle, University of Bristol Catalytic Self-Replication of Phosphines on Platinum(O)
February 21	Dr C R Pulham , University of Edinburgh Heavy Metal Hydrides - an exploration of the chemistry of stannanes and plumbanes
February 28	Prof. E. W. Randall, Queen Mary & Westfield College New Perspectives in NMR Imaging
March 6	Dr Richard Whitby, University of Southampton New approaches to chiral catalysts: Induction of planar and metal centred asymmetry
March 7	Dr D.S. Wright, University of Cambridge Synthetic Applications of Me2N-p-Block Metal Reagents
March 12	RSC Endowed Lecture - Prof. V. Balzani, University of Bologna Supramolecular Photochemistry

March 13	Prof. Dave Garner, Manchester University Mushrooming in Chemistry
April 30	Dr L.D.Pettit, Chairman, IUPAC Commission of Equilibrium Data pH-metric studies using very small quantities of uncertainpurity

1996 - 1997 (August 1 - July 31)

October 9	Professor G. Bowmaker, University Aukland, NZ Coordination and Materials Chemistry of the Group 11 and Group 12Metals : Some Recent Vibrational and Solid State NMR Studies
October 22	Professor Lutz Gade, University of Wurzburg, Germany Organic transformations with Early-Late Heterobimetallics:Synergism and Selectivity
October 29	Professor D. M. Knight, Department of Philosophy, University of Durham. The Purpose of Experiment - A Look at Davy and Faraday
October 30	Dr Phillip Mountford, Nottingham University Recent Developments in Group IV Imido Chemistry
November 12	Professor R. J. Young, Manchester Materials Centre, UMIST New Materials - Fact or Fantasy? Joint Lecture with Zeneca & RSC
November 13	Dr G. Resnati, Milan Perfluorinated Oxaziridines: Mild Yet Powerful Oxidising Agents
November 18	Professor G. A. Olah, University of Southern California, USA Crossing Conventional Lines in my Chemistry of the Elements
November 19	Professor R. E. Grigg, University of Leeds Assembly of Complex Molecules by Palladium-Catalysed Queueing Processes
November 27	Dr Richard Templer, Imperial College, London Molecular Tubes and Sponges
December 3	Professor D. Phillips, Imperial College, London "A Little Light Relief" -
December 11	Dr Chris Richards, Cardiff University Sterochemical Games with Metallocenes

January 16	Dr Sally Brooker, University of Otago, NZ Macrocycles: Exciting yet Controlled Thiolate Coordination Chemistry
January 21	Mr D. Rudge, Zeneca Pharmaceuticals High Speed Automation of Chemical Reactions
February 4	Dr A. J. Banister, University of Durham From Runways to Non-metallic Metals - A New Chemistry Based on Sulphur
February 18	Professor Sir James Black, Foundation/King's College London My Dialogues with Medicinal Chemists
February 26	Dr Tony Ryan, UMIST Making Hairpins from Rings and Chains
March 4	Professor C. W. Rees, Imperial College Some Very Heterocyclic Chemistry

Posters of some of this work was presented at

- ICI Poster Competition, Durham University, December, 1996.
- ISIC 97, University of Edinburgh, August, 1997.

Presentations of some of the work have been made to Britmag Ltd. over the course of the project.