# Studies on the precipitation of metals by magnesium hydroxide

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# *Studies on the Precipitation of Metals by Magnesium Hydroxide.*

by

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September
1994

***To Mum and Dad***

***MY FIRST BOOK*** ☠

# *Declaration.*

The work described in this thesis was carried out in the University of Durham between October 1993 and September 1994. 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.

# *Acknowledgements.*

| | |
|---|---|
| **Redland Magnesia Products** | For funding this M.Sc. project. |
| **Dr. K. B. Dillon** | For encouragement and for putting up with me and my constant whining throughout the year |
| **Mr. R. J. Foreman** | For support from the company at the initial stages of the project. |
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| **Penny, Leela, Tom Richard, Graham, Gazza, Gavin** ☺ | For making the lab an infinitely more difficult place to work! |
| **Simon, Alex, Jon Helen, Rory** ☺ | For constant abuse at coffee time. |
| **Vanessa** | Making life more enjoyable, like only she knows how! |

(Penny says "oo er!" ☺ ☺ )

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# *Abstract.*

Industrial waste has historically been treated with a number of alkalis, the purpose of which is to lower the concentration of metals dissolved in the waste below a certain level, imposed by regulatory bodies, for discharge into the nation's water systems. The alkalis most commonly used are sodium hydroxide, sodium carbonate and lime.

Magnesium hydroxide is now being considered as an industrially viable alternative to these alkalis. Among the advantages of magnesium hydroxide are cost, manageability and safety considerations, sludge settling times and waste volumes.

Redland Magnesia Products (previously Steetley Magnesia Products) have been producing magnesium hydroxide for many years, mostly to produce high temperature resistant bricks, used in kilns and furnaces. In the past few years the company has started to produce "Neutramag"; a concentrated slurry of magnesium hydroxide in water.

However, the company has had problems precipitating certain metals from samples of industrial waste streams. The problem is of great concern as it is preventing them selling the product to many potential buyers. This project, and the work therein, was initiated by the company in the hope of understanding the problem at hand and hopefully producing a solution to the problem.

Reactions were performed firstly on single metal solutions of zinc and nickel (two of the "problematic" metals) and then on mixtures of the two. Initially magnesium acetate was added to the solution in the expectation that the acetate ions would form some acetic acid *in situ* and thus form a buffer solution. Although the addition of acetate ions did have an effect on the reaction it was not due to any buffering action. Then different metal acetates were used to see if the effect was general or specific to magnesium acetate.

Ammonium acetate gave the best results of any of the acetates tried and so ammonium nitrate was added to the reaction to see if it was the acetate or the ammonium ions that were causing the effect. This reaction was successful, and it was realised that in the reaction conditions, ammonia would be generated, which could act as a ligand to the metals. Hence the idea of the "ligand" effect was generated.

Other ligands were added (organic and inorganic) and there was a direct correlation between the rate of reaction and the position of the added ligand in the spectrochemical series, acetate < ammonia < TMEDA < 2,2-bipyridine < $PPh_3$. The best ligand was found to be triphenylphosphine. The studies were extended to some real industrial waste samples supplied by Redland, several of which contained large quantities of iron. The addition of $PPh_3$ showed another effect on the addition of Neutramag to a dilute iron (II) solution. The precipitate was iron (III), the addition of the ligand having increased the rate at which the iron (II) was air oxidised.

Oxidation of iron (II) to iron (III) helps precipitation as the solubility product of the hydrated oxide of iron (III) is much smaller than that of iron (II). Air will oxidise iron (II) although this process can be speeded up by aerating the solution. This, along with the addition of $PPh_3$, was found to increase the rate of reaction significantly. A considerable improvement in clean-up of waste samples, compared with previous results has been achieved.

As the supply of industrial waste was small, a generic waste was made up with a constitution close to that of one of the more concentrated iron wastes. It was shown that due to the insolubility of $PPh_3$ there is direct reaction of the solid ligand with the metal ions in the solution. Brief attempts were made to try and introduce the ligand into the reaction by different methods in the hope of increasing the rate even further.

# Chapter 1

# Introduction

## 1.1 The Beginning.

The purpose of this project is to try and assist Redland Magnesia Products with one of their industrial processes. This introduction is a quick *résumé* of the problems encountered by Redland and a description of the product and the reasons for selling it.[1]

## 1.2 Advantages of magnesium hydroxide over other alkalis.

Many alkalis are used for environmental control purposes, e.g. in processing, in waste water and effluent treatment and in flue gas desulphurisation. The most commonly used 'traditional' alkalis are lime, sodium hydroxide and sodium carbonate. The widespread location of limestone deposits, makes lime, calcium oxide CaO and calcium hydroxide $Ca(OH)_2$ the most used alkalis. It is readily available and has a history of usage.

Sodium hydroxide (NaOH) and sodium carbonate ($Na_2CO_3$) are also used in quantities, but either sourced naturally or by synthesis are relatively expensive. Magnesium hydroxide $Mg(OH)_2$ whilst only used selectively in recent years, is now recognised as having significant technical and cost advantages.

The magnesium hydroxide used in the project was used in the form sold by Redland under the trade name of Neutramag.

**NEUTRAMAG is an aqueous suspension of magnesium hydroxide.**

It is produced by burning dolomite to produce 'Dolime' and reacting this with sea water to precipitate magnesium hydroxide.

$$CaO.MgO + MgCl_2 + 2H_2O + MgSO_4 \longrightarrow \underset{\text{'Neutramag'}}{2Mg(OH)_2} + CaSO_4 + CaCl_2$$

$$\text{Dolime + magnesium salts in sea water} \longrightarrow \underset{\text{hydroxide}}{\text{Magnesium}} + \underset{\text{spent sea water}}{\text{Calcium salts in}}$$

Magnesium hydroxide is sparingly soluble in water and thus a solution of $Mg(OH)_2$ in water does not reach high pH levels. Even in excess (a saturated solution) the maximum pH of Neutramag is approximately 10.5. The lower final pH achieved also causes the precipitation reaction to be slowerthan for the other hydroxides in use, generally producing larger crystals. This can give lower sludge volumes which can be more readily filtered, producing a drier, more manageable residue for disposal. This would also reduce landfill costs as the volume of solid for a specific mass of hydroxides would be lower than that for lime or sodium hydroxide.

Magnesium hydroxide is much safer, from a heath and safety point of view, to handle than lime or sodium hydroxide. By comparison, lime and sodium hydroxide are very reactive with water and liberate heat on dissolution, requiring stringent safety precautions during handling and use. They both also form strongly alkaline solutions in water and are corrosive, unlike magnesium hydroxide.

Neutramag magnesium hydroxide is classified as a slightly soluble base, and since it is in the form of a slurry, the problems of wetting and hydration are avoided.

### 1.3 The application of Magnesium hydroxide to waste water treatment.

The following sections are taken from a report written in 1992 by Mr. R. J. Foreman, and summarise the uses the company had found for the product and the problems encountered which led to this project.[2]

#### 1.3.1 Acid neutralisation.

Figure 1.1 shows a diagram, used in most sales literature from magnesium hydroxide suppliers, showing typical rates of acid neutralisation. Both hydrated lime and sodium hydroxide give a virtually instant increase in pH, but magnesium hydroxide gives a much slower increase in pH. While the latter statement is true, diagrams such as this showing batchwise neutralisations have led to the misconception that magnesium hydroxide reacts very slowly.

Figure 1.2 shows the results of a batch neutralisation of 0.03M sulphuric acid using a stoichiometric addition of magnesium hydroxide. Only the data from the first minute of the reaction are considered. (Since pH is defined as minus the logarithm to base ten of the activity of the hydrogen ions present, a knowledge of the hydrogen ion activity coefficient, and dissociation data for the acid, allows the fractional removal of the original acid at a given time to be calculated from the pH at the time. The results of the calculation are shown in Figure 1.2.)

Clearly after only 20 seconds of reaction virtually all of the acidity has been removed, although the pH is below pH 4 , and therefore by stoichiometry virtually all of the magnesium hydroxide must have reacted. Hence magnesium hydroxide may not give the instant pH response of hydrated lime or sodium hydroxide, but it still very rapidly removes acidity.

**Figure 1.1 : Typical rates of acid neutralisation**

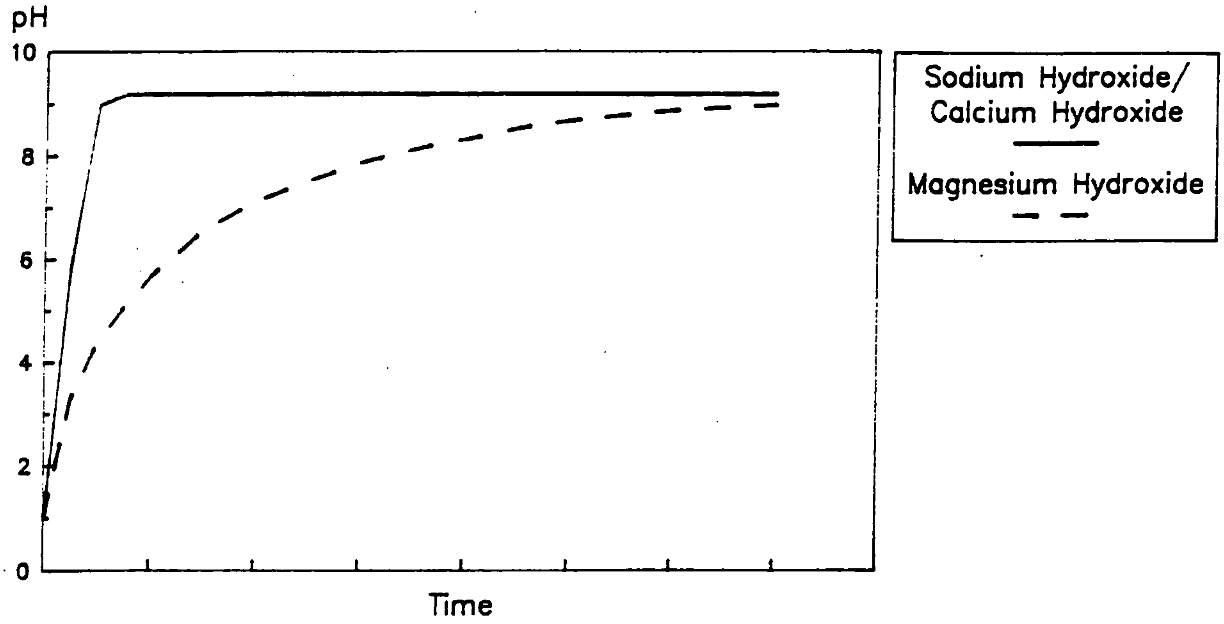
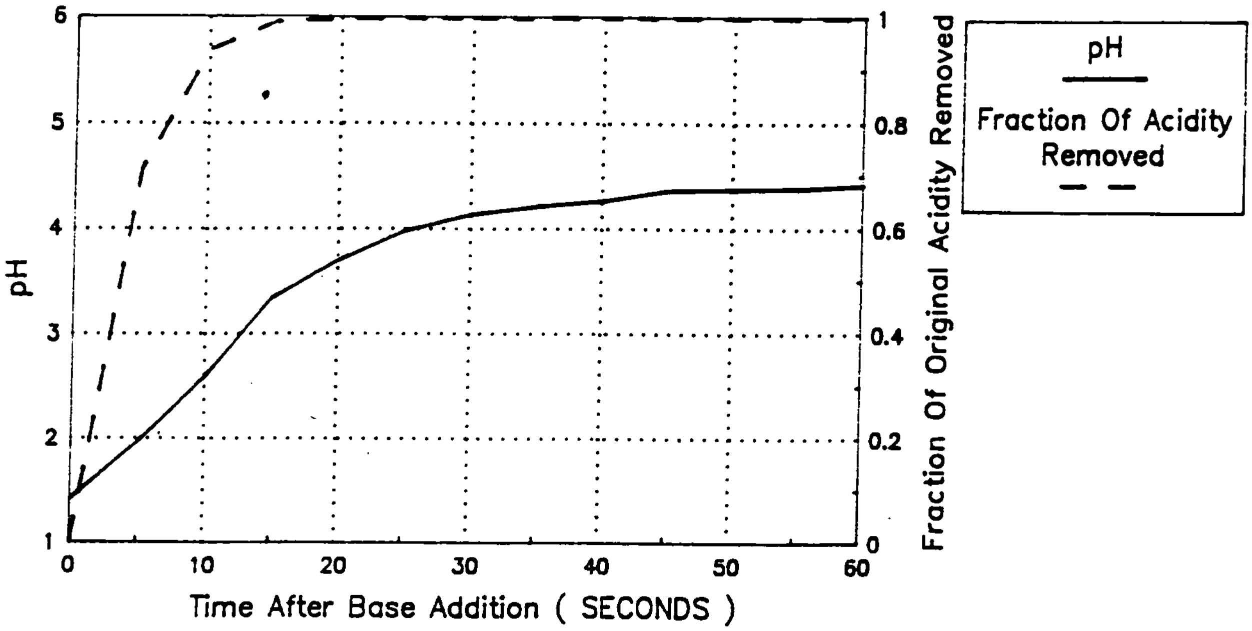


**Figure 1.2 : Batch neutralisation of 0.03M Sulphuric acid**

pH and fraction of original acidity Vs. Time



### 1.3.2 Precipitation of metals.

#### 1.3.2.1 Effectiveness.

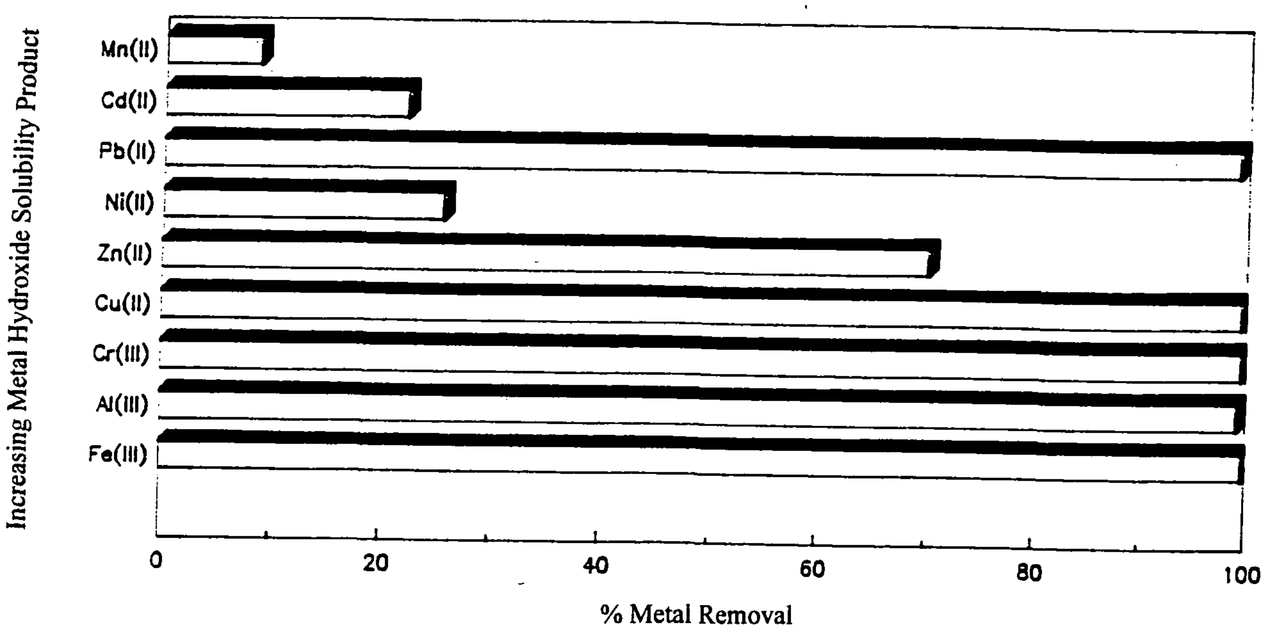
When considering any alkali for use in a treatment system where precipitation of metals is of concern, the first requirement is likely to be that the alkali is capable of removing sufficient metal ions from solution so that the discharge constraint imposed by regulatory bodies can be satisfied. This section outlines some general guidelines as to what can be expected when using magnesium hydroxide. However, since many trade effluents contain diverse mixtures or metals and other species, it is recommended that individual cases are treated on their own merit, since an interactive effect between species can lead to anomalous results. It should also be noted that the following discussion considers only equilibrium effects, and kinetic effects may influence full scale applications.(*)

*(NB As it turned out over the length of the project the previous comment was very apposite.)

Figure 1.3 shows the percentage removal of various metals from a solution containing 20 ppm of each metal (ppm = parts per million or mg/litre), after the pH of the solution was adjusted to pH 7 using magnesium hydroxide. Figure 1.4 shows the same data, but in this case the percentage removal of each metal is plotted against the solubility product of its hydroxide. The metals with very low solubility products have been completely removed (e.g. $Fe^{3+}_{(aq)}$), whereas the others have been removed in proportions related to the magnitude of the solubility products, although nickel and lead do not seem to fit the relationship.

**Figure 1.3 : Percentage metal removal from solutions containing 20 ppm of various metals.**

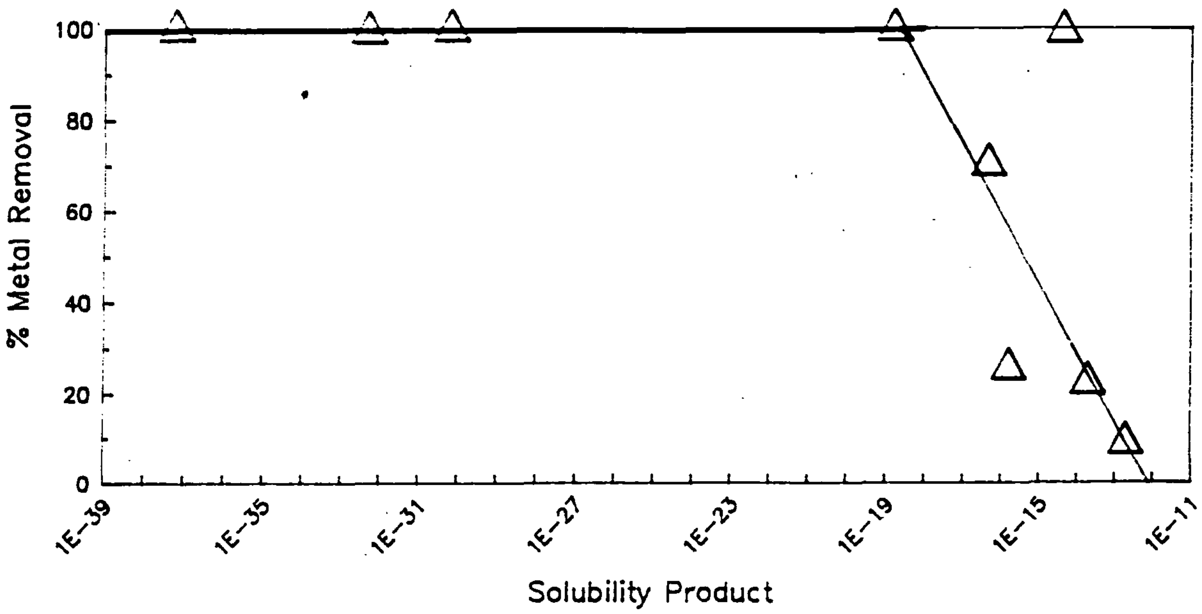
Solution adjusted to pH using magnesium hydroxide



The data presented in Figure 1.4 lead to a general "rule of thumb" relating to precipitation of metals using magnesium hydroxide. Divalent metals with solubility products of less the $1*10^{-18}$ can be completely removed by neutralisation to pH 7, whereas those with solubility products greater than $1*10^{-18}$ will not be completely removed. (For trivalent metal ions an equivalent figure would be approx. $1*10^{-24}$.). That is not to say that these metals cannot be removed, but that a stoichiometric excess of magnesium hydroxide is required to give pH values higher than 7.

**Figure 1.4 : Percentage metal removal Vs. Solubility product of metal hydroxide**

Solution adjusted to pH 7 using magnesium hydroxide



NOTE – Starting solution contained 20 ppm. of each metal

Table 1.1 gives a list of solubility products for common metal hydroxides. Copper and the metals below it are easily removed at pH 7, whereas those above zinc in the list require higher pH values. Note also that oxidation of Fe (II) to Fe (III), usually achieved by aeration, will allow removal of iron at lower pH than would otherwise be necessary. (If the iron (II) is oxidised to iron (III), however, more Neutramag is of course needed for the precipitation).

**Table 1.1**

**Solubility products for metal hydroxides.**[3]

| Hydroxide | Solubility-Product constant |
|---|---|
| $Mg(OH)_2$ | $1.1 * 10^{-11}$ |
| $Mn(OH)_2$ | $2.0 * 10^{-13}$ |
| $Cd(OH)_2$ | $2.0 * 10^{-14}$ |
| $Pb(OH)_2$ | $4.2 * 10^{-15}$ |
| $Fe(OH)_2$ | $7.9 * 10^{-16}$ |
| $Zn(OH)_2$ | $2.0 * 10^{-17}$ |
| $Ni(OH)_2$ | $6.5 * 10^{-18}$ |
| $Cu(OH)_2$ | $1.6 * 10^{-19}$ |
| $Cr(OH)_3$ | $1.0 * 10^{-33}$ |
| $Al(OH)_3$ | $1.0 * 10^{-33}$ |
| $Fe(OH)_3$ | $2.0 * 10^{-39}$ |

Units are : $mol^3dm^{-9}$ for $M^{2+}$

$mol^4dm^{-12}$ for $M^{3+}$

Figures 1.5 and 1.6 show the results of a series of experiments on the precipitation of chromium and zinc, from solutions containing 0.5g metal/litre, using magnesium hydroxide. Each point on these graphs represents an individual experiment allowed 30 minutes for reaction, in an attempt to achieve equilibrium conditions. The results support the "rule of thumb" discussed earlier, i.e. stoichiometric magnesium hydroxide addition completely removes chromium from solution at pH 7, but a stoichiometric excess of magnesium hydroxide was required to achieve precipitation in the case of zinc. Note also that these results demonstrate the buffering effect of magnesium hydroxide, when excess is added, at pH 9 - 9.5.

(What the company's paper means by the term buffering is not in the true chemical sense i.e. a buffer solution is a solution of a weak acid or base and a salt thereof which remains approximately constant in pH when small amounts of acid of alkali are added, but the phenomenon in which it is referred to above, arises from the common ion effect. This comes about because magnesium hydroxide is sparingly soluble. As the metal ions are precipitated out of the solution they are replaced by magnesium ions, and the more magnesium ions that are present in the solution the slower the solid magnesium hydroxide will dissolve, up to a point where a saturated solution of magnesium hydroxide is produced. [As pointed out earlier, Neutramag itself is a saturated solution of magnesium hydroxide]. The pH of the slurry is approximately 10.3, but the maximum pH attainable in the reactions is not as high as this because magnesium ions are already present in the solution combined with anions other than hydroxide, introduced by the metal salts; such as chloride, sulphate etc. Since the solubility product of $Mg(OH)_2$ is dependant on the concentration of hydroxide ions [see equation 1], the equilibrium constant is limited by the common ion effect. The maximum concentration of hydroxide ions present is only great enough to raise the pH to 9 - 9.5).

Figure 1.5 : Precipitation of chromium using magnesium hydroxide

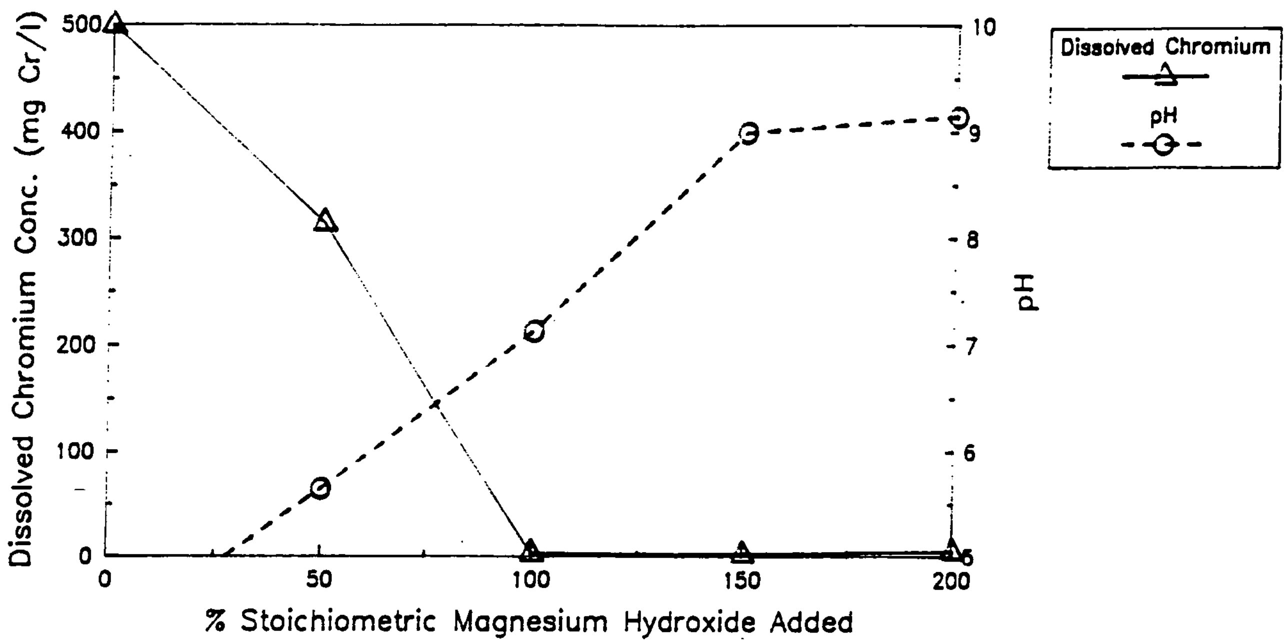
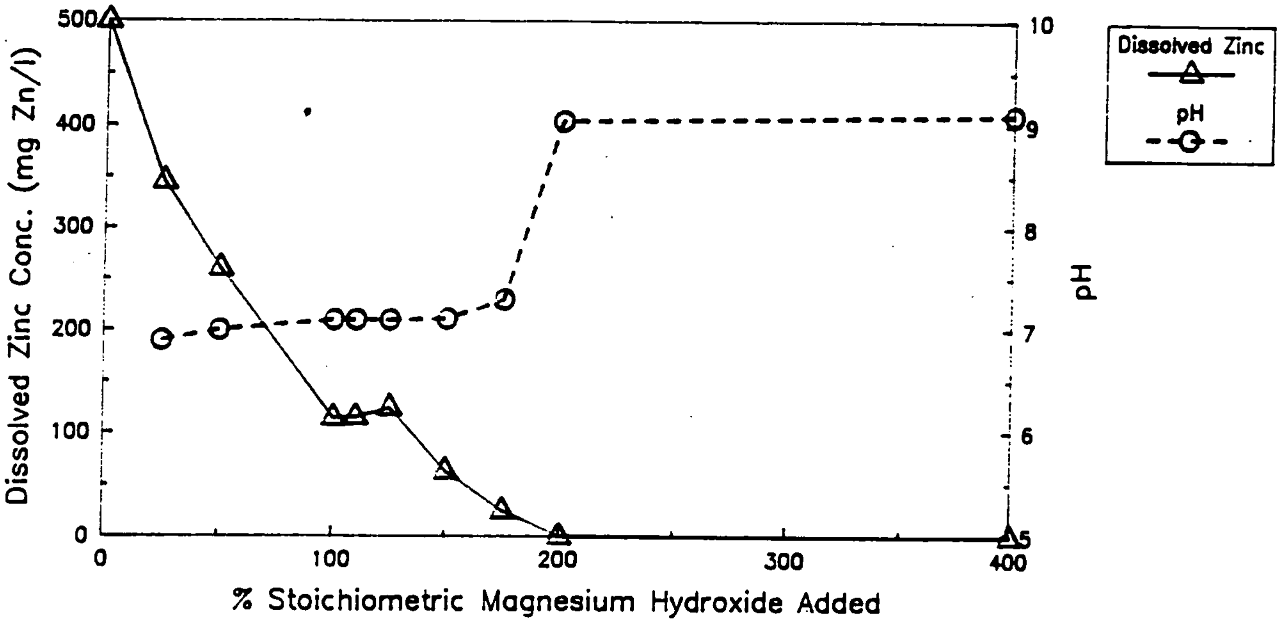


Figure 1.6 : Precipitation of zinc using magnesium hydroxide



However, when complex mixtures of metals are being treated the picture becomes more clouded. In some instances the solution will buffer at a pH which is too low to achieve complete metal removal, nickel being a metal prone to this effect.

(The work done in this thesis shows that this is not an accurate statement. The solution does not "buffer" at a lower pH. What actually happens is that in 30 minutes the reaction has not gone far enough for the pH to rise sufficiently. The problem is a kinetic one, and not due to the "buffering" of the magnesium hydroxide. [See 3.6])

In many cases this can be overcome by using significant excesses of magnesium hydroxide, although process economics can become unattractive in these circumstances. Alternatively, there are occasions when significant metal removal occurs at a pH lower than would normally be required. It is suspected that this is due to co-precipitation with other metals that are being removed at the lower pH values. Conversely, when excess magnesium hydroxide leads to further metal removal, the mechanism is thought to be adsorption onto the surface of the undissolved magnesium hydroxide.

**Solubility product of magnesium hydroxide.**

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

**Equation 1**

Table 1.2 gives an example where magnesium hydroxide was used to treat an industrial effluent sample which was heavily contaminated with metals. Metal removal efficiencies ranged from 95% for manganese up to 100% for iron. In this case removal of more than 99% of nickel in the original solution was achieved at pH 8, although the discharge level of <5ppm was not achieved. It is surprising that so much of the nickel was removed at this pH (in fact a slightly higher addition of magnesium hydroxide gave essentially total metal removal) since experiments on solutions containing only nickel suggested that a much higher pH was required. The example serves to illustrate the point made earlier - each effluent should be assessed on an individual basis.

(Because of this project more is now understood about the factors that affect the precipitation of nickel and iron (II), although co-precipitation has not been studied due to time constraints.)

**Table 1.2**

| | Raw effluent | After treatment to pH 8 using $Mg(OH)_2$* | |
|---|---|---|---|
| Metal | Metal ion conc. (mg/l) | Metal ion conc. (mg/l) | % metal removal |
| Nickel | 2290 | 15.90 | 99.30 |
| Chromium | 955 | 0.19 | 99.98 |
| Cadmium | 1.83 | 0.03 | 98.40 |
| Copper | 7.70 | 0.24 | 96.90 |
| Lead | 7.05 | 0.31 | 95.60 |
| Zinc | 15.90 | 0.09 | 99.40 |
| Manganese | 79.20 | 4.11 | 94.80 |
| Iron | 12,330 | 0.15 | 99.99 |
| Aluminium | 62.70 | 0.41 | 99.30 |

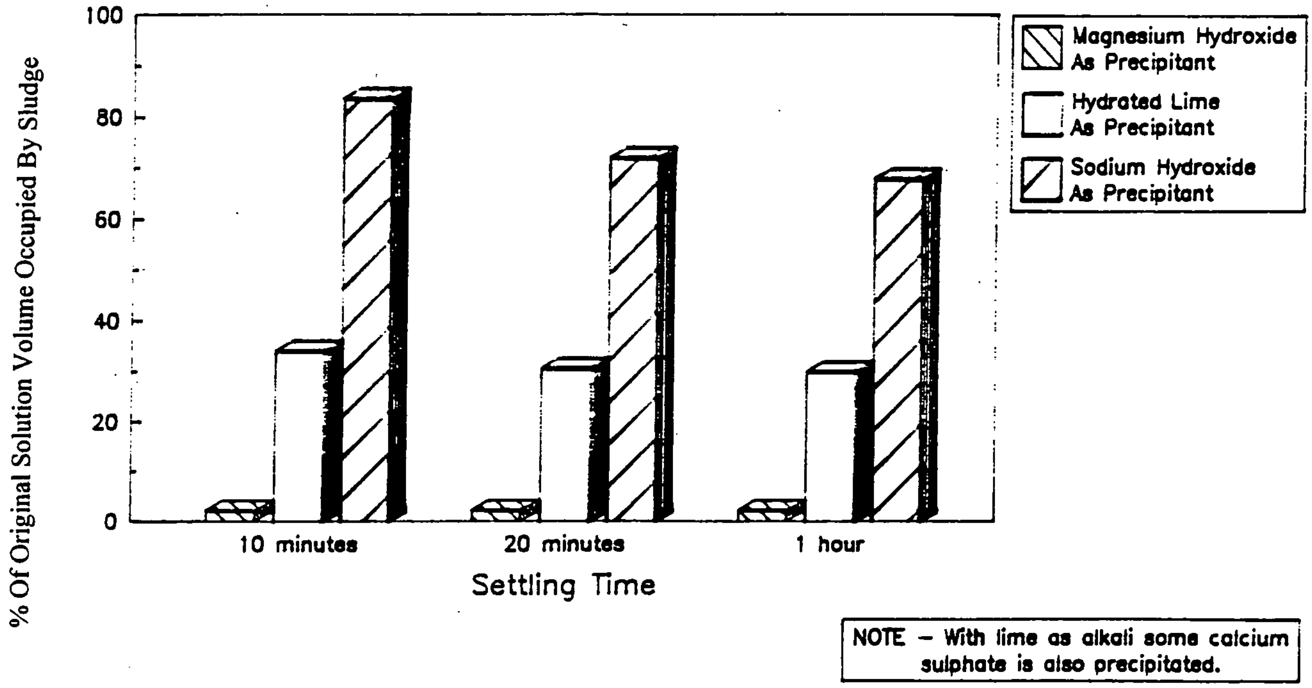
* A slight stoichiometric excess was needed to give a pH of approximately 8

### 1.3.2.2 Precipitation characteristics when using magnesium hydroxide.

Figure 1.7 shows a comparison of the sludge volumes produced when copper hydroxide is precipitated using different alkalis. The interesting point to note here is that not only is the sludge volume produced by magnesium hydroxide significantly lower than with the other alkalis, but it is compacted to its final volume in a much shorter time. With magnesium hydroxide, the precipitate has settled to its final volume in under ten minutes, whereas with the other alkalis, a longer period is needed. This illustrates the gelatinous nature of the precipitates when using hydrated lime and sodium hydroxide. Clearly the use of magnesium hydroxide will lead to improvements in operating efficiency of solid-liquid separation equipment such as clarifiers.

**Figure 1.7 : Sludge volumes for copper precipitation**

From copper (II) sulphate solution at 1g Cu/l



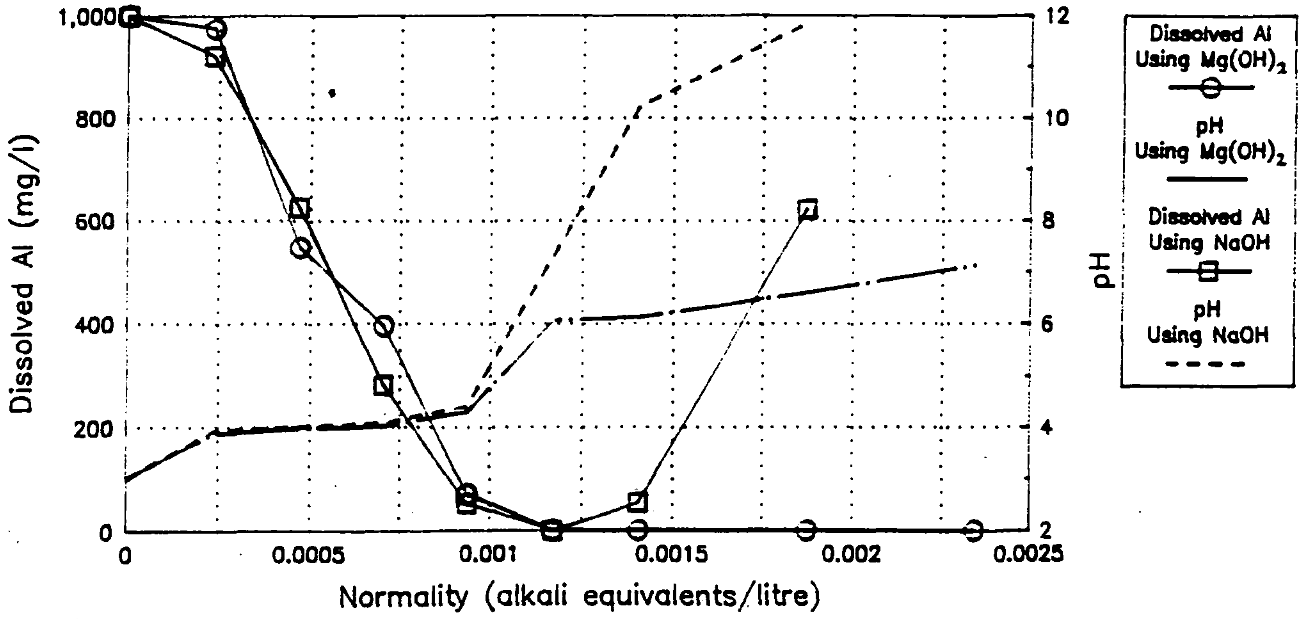
### 1.3.2.3 Overdosing effects.

If accidental overdosing of sodium hydroxide or calcium hydroxide occurs in the presence of precipitated metal hydroxides, some of the metals may redissolve. The extent of redissolution will vary from metal to metal, and will depend on the pH attained. In many cases the effect will be insignificant, as is the case with manganese. However, in some cases redissolution could lead to failure to satisfy discharge consents. The "buffering effect" of magnesium hydroxide at pH 9 - 9.5 (if overdosed) would be an advantage in preventing such occurrences.

The best example of this effect is exhibited by aluminium hydroxide, because of its amphoteric nature. Figure 1.8 shows the precipitation of aluminium using sodium hydroxide and magnesium hydroxide. In both cases stoichiometric addition causes complete removal of aluminium at approx. pH 7. However, when excess sodium hydroxide is added the aluminium hydroxide redissolved as the complex aluminate ion. The effect of adding excess magnesium hydroxide has no effect on the amount of precipitated aluminium hydroxide.

**Figure 1.8 : Aluminium removal versus alkali addition**

Laboratory prepared solutions



## 1.4 Handling properties of magnesium hydroxide.

Magnesium hydroxide for use in waste water treatment is generally supplied in suspension form. Provided suitable equipment is used to maintain the suspension, the material can be pumped and dosed in the same way as a liquid, although appropriate pumps and valves must be used. There are no problems with heat release associated with contacting calcium oxide or sodium hydroxide with aqueous systems, and because of the low solubility of magnesium hydroxide the suspension will not freeze above 0°C. In contrast, 47% sodium hydroxide solution, the strength at which it is normally supplied, will freeze at 8°C. In fact a slight variation in strength, either above or below 47%, will cause the freezing point of caustic soda to be higher still. The use of magnesium hydroxide lessens the need for heated storage tanks and trace heating of pipework.

Suspensions of magnesium hydroxide can be handled with only the minimum of safety precautions, whereas protective equipment is required for the handling of lime of caustic soda, which can cause severe skin and eye damage. The innocuous nature of magnesium hydroxide is demonstrated by the fact that a pharmaceutical grade is sold as a remedy for acid indigestion

## 1.5 Conclusion.

While in certain applications magnesium hydroxide may prove to be unsuitable, in the majority of cases it offers a cost effective alternative to other alkalis. It is much safer to handle than sodium hydroxide or lime, offers better pH control if used in a suitable system, and can lead to significant reductions in landfill costs when used in treatment processes where sludge is produced for disposal.

## 1.6 Impressions on the basis for the project.

As shown in this section, there is a problem with the precipitation of certain metal hydroxides; specifically those of nickel, zinc and iron (II). The company initiated this project because they did not employ any one person who could spend time to examine these precipitation reactions in more detail, with a view to improving the efficiency of the process, and an outside investigation seemed desirable.

However there are still many things that have not been covered during the year's work due to time constraints and the proportioning of work to the most important areas. The areas that have not been covered and the areas where it has become apparent that more work needs doing are listed at the end of the thesis in the conclusion.

# Chapter 2

# Experimental

## 2.1 Atomic absorption.

All the experiments using atomic absorption were performed using a Perkin Elmer 5000 Atomic Absorption Spectrometer. All the lamps used in the analysis were Perkin Elmer intensitron lamps.

The main technique used to determine the concentration of metals in a solution is Atomic Absorption. This technique was used throughout the project and the principals of operation are outlined below.[4]

Every element has a specific number of electrons associated with its position in the Periodic Table. The normal and most stable state orbital configuration of an atom is know as the ground state. If energy is applied to the atom, the energy will be absorbed and an outer electron will be promoted to a less stable configuration known as an excited state. Since this state is unstable, the atom will immediately return to the ground state, releasing light energy.

The sample is subjected to a high-energy thermal environment in order to produce excited-state atoms. The environment can be provided by a flame or, more recently, a plasma. However, since the excited states are unstable, the atoms spontaneously return to the "ground state" and emit light. The emission spectrum of an element consists of a collection of emission wavelengths called emission lines because of the discrete nature of the emitted wavelengths. The intensity at an emission line will increase as the number of excited atoms of the element increases.

The process of atomic absorption is illustrated below in Figure 2.1

**Atomic absorption process.**

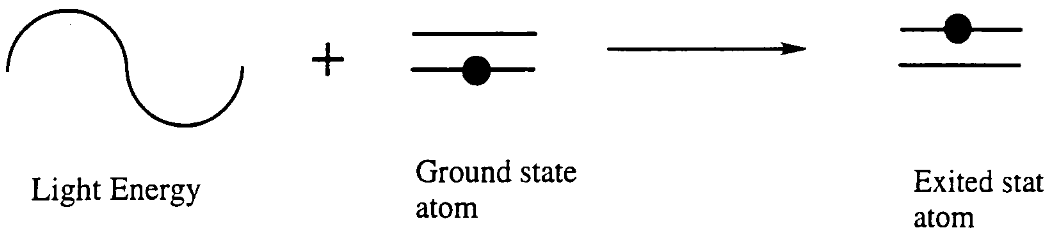


Figure 2.1

The "ground state" atom absorbs light energy of a specific wavelength as it enters the "excited state". As the number of atoms in the light path increases, the amount of light absorbed also increases. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte can be made. The use of specific light sources and careful selection of wavelengths allow the specific determination of individual elements.

The machine itself has specific limits on the concentration of metal in the analyte. This is partially due to the sensitivity of the detector and partly to do with the basic fact that the different metals absorb light energy differently. For example sodium has a very strong absorption/emission band at 589.0 nm (which is the yellow light used in street lamp bulbs). However titanium does not have a strong absorption band and this causes problems with the machine (see later).

In atomic absorption, the only function of the flame is to convert the sample aerosol into atomic vapour which can then absorb light from the primary light source (hollow cathode ray tube or electrodeless discharge lamp).

The absorption spectrum of each metal has many lines in it. In most cases the band which is strongest is the one used. The operator must specify which wavelength is to be used for detection. As there is more than one line in the spectrum, the instruction manual lists all the usable lines, but emphasises the best one.

### 2.1.1 Method of operation.

**Layout for a double beam spectrometer**

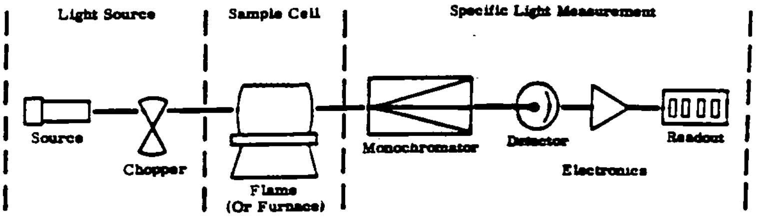


**Figure 2.2**

Each metal has a maximum accurate detection limit. For some metals this is as high as 300-400ppm but for most common metals it is between 1 and 5ppm. The machine has to be calibrated for each metal to be analysed. A cathode ray lamp for the specific metal is placed in the correct position and the light beam shone over the flame.

Deionised water is fed into the machine and this acts as a blank and is set to zero absorption units. The standard is the fed through the machine and the absorption units recorded. Then the machine automatically undertakes a curve correction to make the calibration linear. (see below)

## Curve correction

Quantitative measurements in atomic absorption are based on Beer's Law, which states that concentration is proportional to absorbance (C=kA). However, it is well known that for most elements, particularly at high concentrations, the relationship between concentration and absorbance deviates from Beer's Law and is not linear. Figure 2.3 shows the relationship between concentration and absorbance for nickel.

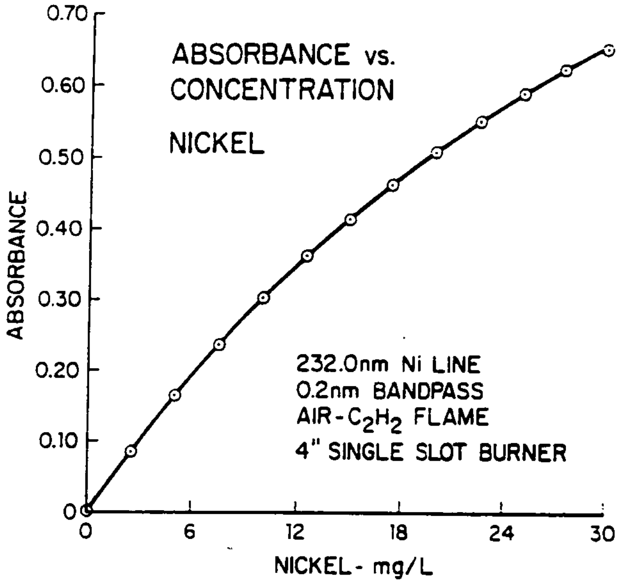


**Figure 2.3**

**Absorbance vs. Concentration for nickel**

There are several reasons for this, including stray light, nonhomogeneities of temperature and space in the cell, line broadening and in some cases overlap of absorptions.

The microprocessor in the machine corrects the curve to be linear between the two points used (zero and the standard). Above the concentration of the standard, a reading on the machine is inaccurate as there is deviation from linearity.

Although the detector records absorption units the machine converts this directly to parts per million and the readings taken from the sample are in ppm. The sample is fed into the flame using the same method as the standard and the readings taken. Three readings are taken to get an average value and to check that the linearity does not drift.

### 2.1.2 Interferences.

There are six major categories of interference in atomic absorption although there is only one which has a major bearing on the project, that of spectral interference:

> "A spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the bandwidth of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal."[4]

Unfortunately the emission/absorption spectrum of titanium is interfered with in this way by many metals e.g. Al, Co, K, Cr, Fe, Li, Zn, Ni, Pb, Na. In the sample under study (See 6.2) titanium is one of the metals present in the original waste. There is also iron in the sample and although in small quantities in the final solution, it does have an interfering effect. Likewise there are large amounts of sodium present in the final solutions, after reaction, as there is a large amount of sodium chloride present in the Neutramag; this will also have an effect. These interferences culminate in the fact that the accuracy at which titanium can be detected is greatly decreased compared to other metals.

## 2.2 Use of pH meter.

Throughout all the reactions the pH was recorded using a Jenway 3020 pH meter and a BDH Gelplas electrode. The electrode was calibrated using pH solutions of 4.0 and 9.2 (at room temp.). The electrode was recalibrated before each reaction and was kept in a solution of approximately pH 1 to remove any hydroxides that had become attached.

## 2.3 Use of heater-stirrer.

During all reactions the solution was stirred using an Ikamay RCT stirrer-hot plate. When the reactions need to be kept at a constant temperature an Ika-tron ETS-D2 temperature probe was used.

## 2.4 Nuclear Magnetic Spectroscopy (NMR)

$^{31}P$ NMR spectra were recorded on a Bruker AC250 machine, operating at 101.256 MHz, using a standard 5mm NMR tube at room temperature (297K). The chemical shift ($\delta$) is measured relative to 85% phosphoric acid, with the higher frequency direction taken to be positive.

## 2.5 Handling and use of Neutramag.

Neutramag is a slurry of magnesium hydroxide in water. It is sold in two forms Neutramag(F) and Neutramag(S); the only difference between the two is that the product is washed in sea water (S) or freshwater (F). The product washed in fresh water (F) is of a higher quality than the (S) because a lot of the sodium chloride is removed.

Most of the reactions in the thesis were performed using Neutramag(F), solely because it is sold as a less viscous slurry and is easier to handle in the lab. All the reactions performed on the industrial and the generic wastes used Neutramag(F). As far as the thesis is concerned the two grades of magnesium hydroxide are considered identical, as the impurities in the Neutramag(S) were not thought to affect the reaction directly.

Although the exact molarity of this slurry varies from batch to batch, the concentration of magnesium hydroxide is approx. 8M. In most of the reactions performed during the project, the concentration of the magnesium hydroxide added was much lower than this for the three following reasons:

1) the slurry of Neutramag is so thick that it is impossible to produce a homogeneous mixture, and as such, two aliquots may not be the same concentration. Dilution was necessary to overcome such problems.

2) Because the slurry is so thick it is impossible to pipette and thus dilution is necessary to accommodate this problem.

3) In the initial reaction the concentration of metal ions in the solution was very small and thus dilution of the Neutramag made addition of the magnesium hydroxide more accurate. The dilutions used are indicated in the appropriate sections.

When the Neutramag was pipetted into the reaction, residual slurry was left in the pipette. This was washed out with water until the pipette was clean.

To calculate the concentration of $Mg(OH)_2$ in the Neutramag slurry, an aliquot is dissolved in a known excess of 1M nitric acid. This solution is then back titrated using 1M sodium hydroxide using phenolphthalein as the indicator. Phenolphthalein is used as the end point of the titration is alkaline.

# *Chapter 3*

# *Initial ideas for the project*

## 3.1 Clearer identification of the problems involved.

### 3.1.1 Starting from the beginning.

It was decided from the outset, that in order to obtain a clearer picture of the complex chemistry involved in treating an industrial waste sample containing several different metals with magnesium hydroxide (Neutramag), it would be necessary first to study the precipitation of single metals separately, in particular those which appeared to be difficult to process. Thus a solution of one of these less tractable metals (e.g. Ni, Zn) was considered to be the best place to start by both Redland and ourselves. Several approaches to the problem were considered, though some were easier to initiate than others.

### 3.1.2 How to approach the problem?

1) When the magnesium hydroxide slurry is added to the metal ion solution, all the dissolved hydroxide (in the slurry) reacts with the metal ions to produce a small amount of precipitate. Then the magnesium hydroxide has to dissolve in the solution for more reaction to occur. If there is some sort of problem with the dissolving of the magnesium hydroxide, one way to solve this problem would be somehow to assist in the dissolution.

   The addition of a Phase Transfer Catalyst (PTC) to organic reactions is well documented.[5] They are used to assist reactions between two phases (either solid-liquid or immiscible liquids) by facilitating passage of molecules from one phase to the other. If there *is* a problem with the dissolution of the magnesium hydroxide then a PTC may help to assist the passage of the hydroxide ions into the solution, and thus increase the rate of reaction.

2) If we assume that the reason for the apparent lack of removal of the metal from the solution is caused by the fact that the pH does not rise to a high enough value, then if we can in some way force the pH of the solution to be higher than it would otherwise be, the problem may be solved.

In all the reports by Redland they state that they normally raise the pH of the test solution to pH 7 and in only a few cases up to pH 8. They state that a small excess of Neutramag has to be added to raise the pH to approx. 8. If this is the case then what is meant by a small excess? As is shown in chapter 4 (4.4.1) even in an excess of 5 : 1 the solution in question ($Zn^{2+}$) still does not achieve a pH of greater that 7.08. In all the later reactions on the industrial wastes, once the pH had risen above pH 8 the reaction went to completion and ended at approx. pH 9.

If an alkaline buffer is added to the solution then the effect may be enough to bolster the pH at a higher value than normal. A phosphate buffer cannot be used, however, as this would precipitate magnesium phosphate, thus defeating the object of the exercise. An acetate buffer is a possible alternative.

If a metal acetate is added to the solution, which is initially acidic, then some acetic acid will be formed *in situ.* A solution containing acetate ions and acetic acid will act as a buffer solution (described in 4.4). Unfortunately, a large amount of acetate would have to be added for this to have a significant effect and the addition of so may new ions to the solution may affect the reaction in other ways.

3) In most kinetic experiments, as a general rule of thumb, if the temperature of the reaction is raised by approximately 10°C then the rate of the reaction will double, e.g. the rate constant, for the hydrolysis of methyl ethanoate, at 35°C is 1.82 times that at 25°C [6].So if we perform the reactions in a solution of approximately 60-70° C then the reaction may be faster (assuming it is a kinetic barrier that is holding up the reaction and not a thermodynamic one). If there *is* a significant increase in the extent of reaction, be it rise in pH or in the percentage of removed metal, then this would suggest strongly that the fundamental problem is a kinetic one and not a thermodynamic one.

## 3.2 Preparations for initial experiments

### 3.2.1 Reasons for initial experiments

After qualitative tests with both zinc and nickel solutions, and using the information provided by Redland, it was decided to concentrate the research on zinc solutions first. This is because zinc only requires a 2:1 excess of Neutramag whereas the nickel requires a much larger excess and therefore is harder and more wasteful to dispose of properly.

### 3.2.2 Preparation of a zinc solution

27.98g of zinc nitrate was dissolved in 1000ml of water. This produced a solution of approximately 6000ppm Zn (0.094M solution of $Zn(NO_3)_2.6H_2O$). To make the solution dilute enough to be read on the atomic absorption machine a 20ml aliquot was taken and diluted to 1000ml with water. 2ml of this solution diluted to 250ml gave an AA reading of 0.96ppm Zn.

All the reactions that were performed on zinc were worked up in this way to give a comparison of the concentration with that of the original solution.

### 3.2.3 Preparation of a nickel solution

29.30g of nickel nitrate hexahydrate was dissolved in 1000ml of water. This produced a solution of approximately 5900ppm Ni (0.1115M solution of $Ni(NO_3)_2.6H_2O$).

To make the solution dilute enough to be read on the Atomic Absorption machine a 20ml aliquot was taken and diluted to 1000ml in water. 2ml of this solution diluted to 250ml gave an AA reading of 0.88ppm Ni..

All the reactions done on nickel were "worked up" in this way to give a comparison with the concentration of the original solution.

### 3.2.4 Preparation of a Neutramag suspension

The Neutramag was diluted and the concentration determined as described in Chapter 2.5. A 0.1M suspension was produced and a 20ml aliquot of this was therefore equal to 0.002 moles magnesium hydroxide.

Thus 20ml of the zinc solution and 20ml of the Neutramag suspension gave a reaction in the approximate ratio 1:1.

## 3.3 Reactions of $Zn^{2+}$ and magnesium hydroxide

### 3.3.1 Initial Reactions

Initial reactions of the two combined reagents gave a poor removal of the zinc from solution (12%), and it was decided that the best way to follow the reaction was by using a pH meter. However the two solutions did not occupy enough volume (40ml) for the pH electrode to read the pH properly. Thus approximately 500ml of de-ionised water was added to the original reaction mixture and at the end of the reaction, the solution made up to 1000ml.

While dilution may speed the reaction, as there is more volume for the magnesium hydroxide to dissolve, the number of moles reacting remains constant, so it was decided that this was nothing to be concerned about.

The reaction was followed using a pH meter and the mixture was left to equilibrate at a certain pH before proceeding, at each stage. It was found that even with an excess of Neutramag the pH of the reaction did not rise above pH=7.1 (Table 3.1)

**Table 3.1**

| volume Neutramag added (ml) | 0 | 5 | 10 | 15 | 20 | 40 | 60 | 80 |
|---|---|---|---|---|---|---|---|---|
| pH | 5.30 | 5.8 | 6.95 | 6.99 | 7.01 | 7.04 | 7.07 | 7.08 |

One possible reason for the stabilisation of the pH could be the complexation of the zinc hydroxide with more hydroxide ions (see below). This, however, is unlikely as in an alkaline solution complexation only occurs in concentrated excess alkali.[7]

$$Zn(OH)_2 + 2OH^- \longrightarrow [Zn(OH)_4]^{2-}$$

### 3.3.2 Reactions involving a phase transfer catalyst

In organic chemistry a Phase Transfer Catalyst (PTC) is used to transfer molecules between two phases that would not otherwise react. The same may be true of the magnesium hydroxide reactions. If there is a problem in transfer of the hydroxide ions from the solid to the liquid phase, then the PTC might facilitate the passage of the hydroxide ions into the solution.

Reactions were attempted using the PTC (as below) in a purely aqueous solution. There was no visible difference in the reaction or in the percentage of the metal removal. The reactions were then repeated, and acetone was added. This was in the hope that the PTC would facilitate passage of the hydroxide ions into the organic solvent and then into the aqueous reaction.

100ml of acetone and a small amount of PTC (tetraethylammonium chloride $(CH_3CH_2)_4N^+Cl^-$) were added to the reaction. Unfortunately a pH electrode is designed to work in an aqueous solution, so the addition of acetone falsifies the pH reading, thus rendering its values useless for this purpose.

Unfortunately the addition of the acetone actually made the reaction worse and the best percentage removal of zinc was 7%.

### 3.3.3 Reaction with excess of Neutramag

To try and get a better understanding of the reaction the 20ml of zinc solution was added dropwise very slowly to 20ml of the Neutramag in the solution. The Neutramag is not very soluble in water (7-8ppm maximum) and thus all the hydroxide in the solution would be reacted instantly. The idea of dripping the zinc solution in slowly is so that more of the unreacted Neutramag will dissolve into the solution, before the next addition of zinc. Thus at a certain point it should be possible to filter the reaction and see when the Neutramag stops dissolving and thus how much of the zinc has reacted.

Initial results showed that approximately 4ml of the zinc solution reacted and then the Neutramag stopped dissolving. After that the pH fell to a constant value and no more zinc was removed.

The zinc was then added in small aliquots to see how the pH responded to the addition. After addition the solution was left for 30 minutes to recover back up to a maximum pH. (Table 3.2)

**Table 3.2**

| Volume zinc solution added (ml) | 0 | 0.9 | 1.05 | 2.8 | 4.0 |
|---|---|---|---|---|---|
| pH | 10.19 | 8.85 | 8.59 | 8.01 | 7.64 |

Percentage Zn removed = 62%

So in fact what we have done here is reacted 4ml of the zinc solution with a 5:1 excess of Neutramag. This was broken down further and only 2ml of the zinc solution were added.

**Table 3.3**

| Volume zinc solution added (ml) | 0 | 1.5 | 1.5 | 2.0 | 2.0 |
|---|---|---|---|---|---|
| time (mins) | 0 | 1 | 75 | 75 | 145 |
| pH | 10.14 | 7.82 | 9.78 | 8.21 | 9.23 |

Percentage Zn removal = 98%

Instead of adding the zinc solution slowly aliquots were added and then the solution left to react.

**Table 3.4**

| Volume zinc solution added (ml) | 2.0 | 2.5 | 3.0 | 3.5 | 10 |
|---|---|---|---|---|---|
| Initial pH after addition of solution | 7.01 | 7.10 | 7.10 | 7.05 | 7.40 |
| Final pH | 9.6 | 9.38 | 9.32 | 9.33 | 9.07 |
| Total reaction time (hours) | overnight | 2 | overnight | 5 | 46 |
| Percentage removal | 96% | 92% | 98% | 98% | 98% |

Thus it would appear that the main problem with the reaction is the kinetics and that the solutions are not left for long enough to react.

## 3.4 Reactions of $Ni^{2+}$ with magnesium hydroxide

Because of the success with leaving the Zn solution to react for a long period of time a nickel solution was reacted in a 2:1 ratio with Neutramag and left over the Christmas holidays. The results (below) illustrated the point that the reason for the problem may well be due to kinetics.

## Table 3.5

| | | | | | |
|---|---|---|---|---|---|
| pH | 7.84 | 7.73 | 7.75 | 7.75 | 7.80 |
| Time | 0 hours | 3 hours | 7 hours | 71 hours | 18 days |

Percentage Ni removed = 48%

# Chapter 4

# Further examination of the kinetics of reaction

## 4.1 Reactions at higher temperatures

As a general rule of thumb for every 10 degrees Celsius the temperature of a reaction is raised, the speed of the reaction doubles. This is true only in the cases where the kinetics are simple. It is however a good basis to start. As the problem with the reactions turned out to be a kinetic one, the best place to start to investigate the kinetics is by varying the temperature.

## 4.2 Addition of "hot" water to the reaction.

As previously described all the reactions were done in approximately 500ml of water so the pH electrode could be used satisfactorily (3.3.1). However in these sets of reactions, approximately 500ml of almost boiling water was added to the mixture of Neutramag and the metals solutions. The absolute volume of the reaction was not considered important and 500ml was an arbitrary value.

The solution was then left to react, but because the reaction was open to the air the solution cooled over the period of the reaction. Whether this has a bearing on the reaction is not easy to show, although, as later results indicate, the lower the temperature of the final solution the higher the pH. In general the higher the final pH of the solution the more of the metal in question is precipitated.

### 4.2.1 Reaction of a zinc solution and Neutramag.

20ml of the zinc solution was placed in a beaker, to this, 500ml of boiling water was added and the solution stirred. 20ml of the Neutramag was added so as to make the reaction in a 1:1.8 ratio. (This was not intended to be the ratio, but after re-determination of the concentration of the Neutramag, it was found that the concentration of magnesium hydroxide had increased due to water evaporation.)

As is shown below (Table 4.1) the speed of the reaction showed a marked improvement from before (Table 3.4) and the reaction was complete in under 2 hours, compared to nearly 24 hours previously.

**Table 4.1**

| pH of solution | 6.14 | 7.03 | 8.43 | 8.43 | 8.43 |
|---|---|---|---|---|---|
| temperature of reaction (°C) | 80.6 | 72.2 | 68.3 | 68.2 (*) | 68.3 |
| time (mins) | 0 | 15 | 105 | 240 | 270 |

Percentage Zn removed = 100%

(*) The reaction was heated to an arbitrary temperature using a heater

### 4.2.2 Reaction of nickel solution and Neutramag

20ml of the nickel solution was placed in a beaker, 500ml almost boiling water was added and the solution was stirred. 20ml of Neutramag was added again to make a ration of 1:1.8 and the solution left to react, with heating at 60°C.

**Table 4.2**

| pH of solution | 6.14 | 7.03 | 8.43 | 8.43 |
|---|---|---|---|---|
| temperature of reaction (°C) | 84.6 | 77.6 | 66.7 | 61.2 |
| time (mins) | 0 | 5 | 100 | 120 |

Percentage Ni removal = >90%

## 4.3 Reaction of solutions containing zinc and nickel with Neutramag

A solution containing 25ml of the zinc solution and 25 ml of the nickel solution was put in a beaker and 500ml of boiling water was added. 50ml Neutramag was added so the reaction was 1:1 in Zn : Mg and 1:1 in Ni : Mg. However this time the results were not so positive and a maximum pH of 6.99 was achieved over 19 hours.

Percentage Zn removed = 49%

Percentage Ni removed = 6%

### 4.3.1 Varying constituents of the zinc and nickel solution

As with the previous experiments, since the main experiment was unsuccessful it was decided to break the reaction down and look at differing compositions of the metals in the hot solution.

According to the solubility products (Table 1.1), zinc hydroxide is more insoluble than nickel hydroxide and thus if the two metals are in the solution with the hydroxide ions then one would expect the zinc hydroxide to precipitate out preferentially. However in the previous experiment only 50% of the metals were removed so there was a large amount of unreacted magnesium hydroxide.

By varying the amount of zinc and nickel in the solution we hoped to gain some sort of insight into why the reaction did not work with both metals present.

## Table 4.3

**Ratio nickel : zinc = 19 : 1**

| pH solution | 6.49 | 6.95 | 7.32 | 8.38 |
|---|---|---|---|---|
| temperature (°C) | 75.0 | 71.4 | 64.7 | 34.3 |
| time (minutes) | 0 | 0 (*) | 45 | 120 |

Percentage Ni removed = >90%

Percentage Zn removed = 96%

(*) In some of the tables recorded in the following sections there are two readings given at time = 0; the first is the pH of the metal mixture in solution and the second one is the initial pH of the reaction after the addition of Neutramag

## Table 4.4

**Ratio nickel : zinc = 17 : 3**

| pH solution | 6.08 | 6.87 | 7.27 | 7.92 | 7.98 |
|---|---|---|---|---|---|
| temperature (°C) | 79.0 | 74.5 | 68.3 | 30.7 | 30.6 |
| time (minutes) | 0 | 0 (*) | 120 | 130 | 140 |

Percentage Ni removed = 61%

Percentage Zn removed = 92%

**Table 4.5**

**Ratio nickel : zinc = 15 : 5**

| pH solution | 6.66 | 7.16 | 7.29 | 7.44 | 7.56 |
|---|---|---|---|---|---|
| temperature (°C) | 70.1 | 44.7 | 32.4 | 31.0 | 30.0 |
| time (minutes) | 0 | 60 | 120 | 130 | 19 hours |

Percentage Ni removed = 27%

Percentage Zn removed = 92%

### 4.4 Addition of magnesium acetate dihydrate $Mg(CH_3COO)_2.2H_2O$

As the pH is vitally important, it was thought that perhaps if some acetate ions were added, they might have a buffering effect on the solution. (°)

Magnesium acetate was used as the acetate (ethanoate) buffers at an alkaline pH. A small excess of Neutramag was used as well to help the precipitation. (The acetate was mixed for 5 minutes with Neutramag and added together)

(° A buffer is a solution of an acid (or a base) and a suitable salt thereof. e.g. acetic acid and magnesium acetate. The pH of a buffer solution is dependent on the composition of the mixture of the two ingredients. As shown in Table 4.7 the pH of a 0.003M solution of magnesium acetate is 7.95.

It was assumed that in the initial reaction when the acetate is added to an acidic solution then some acetic acid would be formed, thus producing *in situ* the constituents of the buffer required).

**Table 4.6**

**Ratio nickel : zinc = 15 : 5**

| pH solution | 6.16 | 6.84 | 7.59 | 7.96 | 8.32 |
|---|---|---|---|---|---|
| temperature (°C) | 74.3 | 71.1 | 66.5 | 43.5 | 29.7(•) |
| time (minutes) | 0 | 0 (*) | 60 | 80 | 105 |

Percentage Ni removed = >90%

Percentage Zn removed = 85%

(•)The reaction was placed in an ice bath to speed up the cooling. As described previously (See 4.2), the lower the temperature, the higher the pH seemed to be, and the higher the pH then the more likely that metals had precipitated out.

The percentage removal of nickel in this reaction seemed a little anomalous when the reaction was repeated, but gave hope and encouragement. The normal value for the removal was about 50% but this was still twice as good as reported by Redland.

### 4.4.1 Precipitation of zinc hydroxide.

The precipitation of the zinc hydroxide can be seen in several forms. If the solid is precipitated from the solution slowly then all that is seen is a small grain granular precipitate. However if the precipitation is fast then a "fluffy" colloidal precipitate is observed. The reason for this is not fully understood.

This does have a major bearing on the project, though. It appeared that the fluffier the precipitate the better the yield of the hydroxides and this was a good rule of thumb to use, to see whether or not the experiment was working as desired.

### 4.5 Use of other metal acetates.

Originally magnesium acetate was used so that no other metals were introduced into the experiment, thus complicating matters. But at this point it was decided to try other metal acetates so see whether or not the reaction was dependent on specific metals.

The pH of each of a 0.003M solution of the acetates in water was determined to see whether or not this had a bearing on the reaction. 0.003M was an arbitrary value and in the reaction concerned this meant a ratio of approximately 1 : 3 of the acetate to the Neutramag.

The results of the reactions done are shown below (Table 4.7)

**Table 4.7**

| Acetate | pH of 0.003M solution. | Percentage Zn removed | Percentage Ni removed |
|---|---|---|---|
| $Mg(OAc)_2$ | 7.95 | 90% | 48% |
| LiOAc | 8.01 | 37% | 7% |
| NaOAc | 8.32 | 65% | 23% |
| $NH_4OAc$ | 7.01 | 94% | 86% |
| $Cu(OAc)_2$ | 6.15 | 2% | 15% |
| $Ni(OAc)_2$ | 7.96 | 47% | 73% |
| $Pb(OAc)_2$ | 6.60 | nominal | nominal |
| $Mn(OAc)_2$ | 7.67 | nominal | nominal |
| $Mg(OAc)_2$+$NH_4OAc$ | 7.08 | 95% | 91%(*) |
| $Na(ClCH_2COO)$ | 7.69 | nominal | nominal |

(*)Result was obtained under different reaction conditions to others in table (see later)

The result for the $NH_4OAc$ was very promising as the precipitate was the most colloidal of any of the reactions. Thus it was decided to pursue the reaction with ammonium acetate.

### 4.6 The use of cooling in the reaction.

As was pointed out earlier (4.2), the colder the final temperature of the reaction the higher the pH and thus the higher the yields of the required hydroxides. This was achieved by placing the reaction mixture into an ice bath and leaving it to cool for 20 minutes.

### 4.7 Variation of the amount of ammonium acetate added.

As with any kinetic experiment in which a catalyst is being used (on the assumption that the acetate has catalytic qualities), the amount of the catalyst added should vary the speed of the reaction up to a point where further addition causes an overdose and effects no further increase in the reaction rate. Thus various reactions were carried out, varying the amount of $NH_4OAc$ added to see if this hypothesis held.

Although variations in the amount added to the reaction did show a change in the pH of the final solution and therefore the amount of hydroxide precipitated, this change was not linear and showed no clear trend.

### 4.8 Use of ammonium acetate in conjunction with magnesium acetate

Because the most positive results were seen with the magnesium acetate and the ammonium acetate in separate reactions, reactions containing both salts were tried. The composition of the added acetates was varied to try and obtain the best reaction conditions. (Table 4.8)

**Table 4.8**

| Moles $NH_4OAc$ added | Moles $Mg(OAc)_2$ added | final pH of the solution | Percentage Zn removed | Percentage Ni removed | final temperature solution(°C) | time (hours) |
|---|---|---|---|---|---|---|
| 0.0015 | 0.0034 | 7.80 | 83% | 45% | 10.0 | 20 |
| 0.0037 | 0.0048 | 8.97 | 95% | 91% | 6.50 | 5 |
| 0.0024 | 0.0071 | 8.67 | 100% | 86% | 16.2 | 4 |
| 0.0130 | 0.0008 | 8.87 | 95% | 91% | 5.7 | 3.75 |
| 0.0071 | 0.0103 | 9.01 | 95% | 92% | 7.3 | 1.5(*) |
| 0.0071 | 0.0067 | 8.89 | 100% | 87% | 5.3 | 1.17(*) |

(*)Although there is no significant mixture that stands out as being the best it is noticeable that the more acetate that is introduced to the reaction the faster the rate.

## 4.9 Addition of magnesium nitrate and ammonium nitrate.

These results pose the question is it the acetate ions that are affecting the reaction or is it the $Mg^{2+}$ and the $NH_4^+$ ions in the solution? So a comparative reaction was set up using magnesium nitrate and ammonium nitrate in comparable quantities. The results are quite startling (Table 4.9), even more so as the reaction was just left to cool down and was not placed in ice!

Table 4.9

| Moles $Mg(NO_3)_2$ added | Moles $NH_4NO_3$ added | final pH of the solution | Percentage Zn removed | Percentage Ni removed | final temperature solution(°C) | time (hours) |
|---|---|---|---|---|---|---|
| 0.0065 | 0.0038 | 8.18 | 100% | 96% | 27.1 | 4.5 |
| 0.0023 | 0.0013 | 8.79 | 78% | 89% | 25.6 | 4.5 |

## 4.10 Addition of ammonium nitrate.

One would assume that the addition of magnesium nitrate, in increasing the number of magnesium ions in the solution, would actually have a detrimental effect on the reaction. The solubility product is dependent on the concentration of magnesium ions.

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

Therefore one could assume that the effect shown in Table 4.9 was due to the ammonium ion in the solution. Thus the experiment was repeated with only the addition of ammonium nitrate and this was the turning point for the project. (Table 4.10)

Table 4.10

| Moles $NH_4NO_3$ added | final pH of the solution | Percentage Zn removed | Percentage Ni removed | final temperature solution (°C) | time (hours) |
|---|---|---|---|---|---|
| 0.0019 | 8.81 | 97% | 89% | 34.4 | 2.2 |
| 0.001 | 8.81 | 100% | 91% | 32.7 | 2.3 |

The major things to note about this particular result are;

i) the fact that without the magnesium nitrate the reaction is faster and gives better yields, confirming the idea that extra magnesium ions hinder the reaction.

ii) The final temperature is still above room temp and thus with more cooling even better yields would be achievable.

Unfortunately the solutions are too dilute to add a significantly smaller amount of ammonium nitrate as 0.001moles = 0.06g. Although smaller quantities could be added by careful dilution of a solution of $NH_4NO_3$ with water.

### 4.11.1 Reaction at room temperature

Reaction at 60°C is not industrially viable and thus the reaction conditions were reversed and "hot" Neutramag was added to a solution of the zinc and nickel at room temperature. (Table 4.11). The Neutramag was heated by the addition of boiling water to the aliquot, before it was added to the reaction.

**Table 4.11**

| Initial reaction temperature | Final reaction temperature | Moles $NH_4NO_3$ added | Percentage Zn Removed | Percentage Ni Removed | Temperature of added Neutramag | time (hours) |
|---|---|---|---|---|---|---|
| 22.0°C | 24.0°C | 0.001 | 98% | 70% | 60°C | 3.1 |

### 4.11.2 Addition of ammonium chloride.

The reaction was repeated except that ammonium chloride was added instead and the Neutramag was added at room temperature as well as being pre-heated.(Table 4.12)

**Table 4.12**

| Initial reaction temperature | Final reaction temperature | Moles $NH_4Cl$ added | Percentage Zn Removed | Percentage Ni Removed | Temperature of added Neutramag | time (hours) |
|---|---|---|---|---|---|---|
| 20.6°C | 23.7°C | 0.002 | 98% | 89% | 78.9°C | 3 |
| 23.1°C | 18.2°C | 0.001 | 98% | 92% | room temp | 48 |

One can see from the table that the addition of the ammonium ions to the solution increased the rate of the reaction from over 20 days (just the Ni solution alone) to 3 days. This suggests that the ammonium ions are possibly facilitating a new reaction pathway, thus affecting the kinetics of the original reaction.

# Chapter 5

# The spectrochemical series

## 5.1 Coordination of ligands to metals in solution.

When dilute ammonium hydroxide is added to a zinc solution, zinc hydroxide is precipitated. However when concentrated ammonia is added the precipitate dissolves again; this is due to the formation of the complex ion $[Zn(NH_3)_4]^{2+}$.

$$Zn^{2+}_{(aq)} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}_{(aq)}$$

So when ammonium ions are added to the solution, one can assume that if the pH of the solution is alkaline (pH > 7.00) then the ammonium ions will react with $OH^-$ ions to generate aqueous ammonia and water.

$$NH_4{}^+_{(aq)} + OH^- \longrightarrow H_2O + NH_{3(aq)}$$

If there is some ammonia in the reaction it would be a reasonable assumption that some of it is going to complex with the zinc. As this is the only other factor outside the original reaction with Neutramag alone, then the reaction should also be affected by other nitrogen ligands such as thiocyanate, phen, bipy etc.

## 5.2 The spectrochemical series

The spectrochemical series is an approximately constant ligand series.[8] The series is one of increasing electrostatic field strengths felt by the *d* electrons in the transition metal concerned. This indicates a series of increasing bond strength between the transition metal and the ligand concerned. The higher the ligand is in the spectrochemical series, the stronger bonds it forms with metals and thus the larger the formation constant of the complex made.[3]

e.g. $Zn^{2+} + 4CN^- \longrightarrow [Zn(CN)_4]^{2-}$ $\log_{10}\beta_4 = 16.7$

$Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$ $\log_{10}\beta_4 = 9.6$

Where $\beta_4$ is the equilibrium constant for the appropriate reaction above.

As shown in the figure below (Figure 5.1), in general a fair approximation is to say that P-donors are better than N-donors, which are better than O-donors for uncharged ligands (P > N > O > S) . Some quantitative work has been done on specific metals and accurate bond strengths etc. can be theoretically calculated for $d^6$ metals.[9]

**Figure 5.1**

$X^- < H_2O < -COO^- < \leftarrow NCS^- < py < NH_3 < TMEDA < en < bipy < phen < PPh_3 < NO_2^- < CN^-$

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

### 5.2.1 Note regarding the previous use and understanding of the action of the acetate ions.

The original idea for the addition of the acetate ions was to try and make a buffering solution to keep the pH of the reaction higher than it would otherwise be. In retrospect what actually happens in the reaction is the acetate ions complex, to a greater or lesser extent depending on the metal, with the metal ions in the solution. Acetate itself is an oxygen donor, although stronger than water, and therefore a "weak" ligand. A ligand is "weak" or "strong" depending on the strength of the bond formed between it and the metal involved (See 5.2)

Because ammonia molecules are nitrogen donors they are better ligands than the acetate ions. Because they make the reaction work faster, one would suspect that the "stronger" the ligand the more effect it will have on the rate of reaction. This statement is true only up to a point. Cyanide ions ($CN^-$) are very strong ligands and it is unlikely that once they have bonded to the metal ion, they will be substituted by the hydroxide ions. This therefore defeats the point of adding them, as they would not have any catalytic effect on the reaction. Cyanide ions also pose a threat as a pollutant and are toxic.

### 5.3 Suspected action of the ligand in the reaction.

There is no doubt that the action of the ammonium ions, and to a lesser extent the acetate ions, are to introduce ligands to the reaction. These ligands then bond to the metal in the solution and displace water molecules from the aquo-complex. e.g.

$$[Zn(H_2O)_6]^{2+} + NH_3 \longrightarrow [Zn(H_2O)_5NH_3]^{2+} + H_2O$$

Once the water complex has been altered by the substitution of the ligand, the new complex must be more susceptible to reaction with the Neutramag. How the reaction is affected is uncertain and a definitive explanation cannot be given on the basis of the data obtained in this thesis, although there are several hypotheses which may account for the observed effects. (See chapter 6)

## 5.4 Addition of sodium thiocyanate (NaSCN)

The thiocyanate ion has a similar complexing ability to ammonia as it bonds through the nitrogen, although there are other factors involved such as the fact that the thiocyanate ligand is charged and ammonia is not (See 5.2). A solution containing a 1:1 ratio of zinc and nickel was placed in 500ml in a beaker and an equivalent amount of "hot" Neutramag was added at about 80°C. The reaction was as shown below (Table 5.2)

**Table 5.2**

**Ratio Zn : Ni = 1 : 1**

| pH of solution | 6.21 | 7.21 | 7.63 | 8.43 | 8.71 |
|---|---|---|---|---|---|
| temperature of reaction ($^{o}$C) | 19.0 | 26.3 | 23.3 | 21.3 | 17.1 |
| time (mins) | 0 | 20 | 100 | 540 | 720 |

Percentage Zn removal = 100%

Percentage Ni removal = 89%

## 5.5 Reaction with Tetramethylethylenediamine (TMEDA)

TMEDA is a better ligand than ammonia as it is a chelating ligand (has more than one complexing atom per molecule). It is a particularly good chelator due to the four methyl groups shared between the two nitrogens. They donate electron density to the nitrogen thus giving it a larger lone pair, making it a better donor of electron density to the metal in question. However TMEDA is a worse ligand than ethylenediamine ($H_2NCH_2CH_2NH_2$) because the methyl groups are a steric hindrance to complex formation.

TMEDA = $[(CH_3)_2N]_2CH_2CH_2$

density = $0.77 g/cm^3$

Therefore $1 cm^3$ = $0.77 g = 6.6 * 10^{-3}$ moles

Therefore 0.2 ml = $1.32 * 10^{-3}$

A solution containing a 1 : 1 ratio of zinc and nickel was reacted with an equivalent amount of Neutramag. To the Neutramag (before it was added to the reaction) was added 0.2ml TMEDA and the solution was stirred. 0.2 ml TMEDA is approximately in the ratio 1 : 2 with each zinc or nickel atom, so not really in a catalytic quantity. But as shown below smaller quantities had similar effects. (Table 5.3)

The results shown in Table 5.3 provide conclusive proof that the ligand is having an effect on the reaction. If more ligand is added then the reaction is faster and better results are obtained. Unfortunately there are hundreds of potential ligands available and the ones that were used in reactions were those already in the laboratory. A more extensive study of varying ligands and metals would give much useful information in any future project.

**Table 5.3**

| Volume TMEDA added (ml) | final pH of the solution | Percentage Zn removed | Percentage Ni removed | final temperature solution (°C) | time (hours) |
|---|---|---|---|---|---|
| 0.01 | 8.59 | 98% | 79% | 17.1 | 24 |
| 0.05 | 8.80 | 98% | 89% | 21.0 | 4.5 |
| 0.10 | 8.85 | 98% | 94% | 20.9 | 2.0 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| 0.20 | 9.09 | 98% | 96% | 25.9 | 40 mins |

This idea of varying the ligands was continued using the industrial samples (Chapter 6).

# Chapter 6

# Industrial waste analysis

## 6.0 Introduction.

This chapter is concerned with industrial waste samples that Redland has not been able to clean up in the past. They all contain some of the metals which have been focused on in previous chapters, e.g. Zinc, Nickel, Iron.

The theory that the ligands play an important role in the equation was continued to be borne in mind whilst working on the industrial samples, and as a result more than one ligand was tried on each of the samples. As will be shown later, it is possible that the best ligand for each metal is not necessarily the same for all.

## 6.1 Industrial waste sample (1)

This solution was supplied by a plating firm and Redland had had problems removing the large amount of iron (II) and the nickel from the solution.

### 6.1.1 Concentrations of the metals in the waste sample.

ppm Zn = 89

ppm Fe = 648

ppm Cu = 177

ppm Pb = 17

ppm Ni = 38

ppm = parts per million = mg/litre

The original solution was diluted 100 times because there was not very much to work with and it made the reaction easier as the metal concentrations were much smaller.

The overall concentration of $M^{2+}$ is $1.65 * 10^{-4}$M

### 6.1.2 New Neutramag slurry.

A new Neutramag slurry was prepared, a solution equivalent to 0.0471M in magnesium hydroxide. In this new case the pH of the initial solution is also quite important. Usually it was approximately pH = 3 which is $1 * 10^{-3}$ moles of $H_3O^+$. This had to be neutralised before any reaction was to take place. (This is not strictly true as some of the precipitates come out of the solution below pH = 7 but we consider that one aliquot of Neutramag is required to neutralise the acid and one aliquot to remove the metals from the solution).

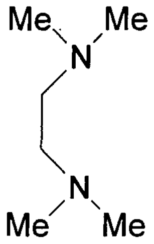
$1 * 10^{-3}$ moles of acid require $5 * 10^{-4}$ moles of Neutramag to neutralise it. Therefore if 20ml of the Neutramag is added to the solution ($9.42 * 10^{-4}$ moles) only approximately $4.42 * 10^{-4}$ moles will react with the metals in the solution. Therefore we have a >2 : 1 ratio of Neutramag to the metals in solution.

### 6.1.3 Preparation of ligands.

Because the concentration of the metals is smaller than previously investigated the concentration of the ligands added has to be diluted accordingly.

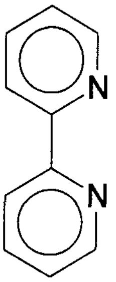
i) 0.1g of ammonium chloride was dissolved in 100ml of water. In the reaction 10ml of this solution when made up to 1000ml would be equal to $1.87 * 10^{-4}$ moles.

ii) 0.1ml TMEDA was make up to 100ml in methanol. 1ml of this solution made up to 1000ml in the reaction would be equal to $6.6 * 10^{-6}$ moles.



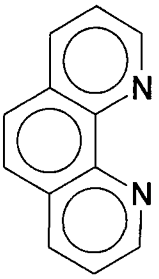
Tetramethylethylenediamine

iii) 0.01g 2,2 bipyridine (bipy) was dissolved in 50ml methanol. In the reaction 0.1ml of this solution when made up to 1000ml would be equal to 1.28 * $10^{-7}$moles.



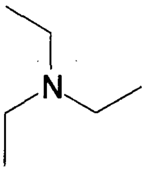
2,2-Bipyridine

iv) 0.1g 1,10-phenanthroline (phen) was dissolved in 100ml methanol and in the solution when made up to 1000ml, 1 ml would be equal to 5.56 * $10^{-6}$ moles.



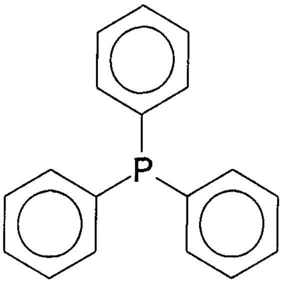
1,10-Phenanthroline

v) Density of triethylamine $[(C_2H_5)_3N]$ is equal to 0.726 (g/$cm^3$) at 298K. Therefore 1ml of this is equal to 0.726g . 1ml was made up to 100ml in methanol. 1ml of this solution used in the reaction is equal to 7.19 * $10^{-5}$moles.



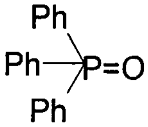
Triethylamine

vi) 0.1g triphenylphosphine ($PPh_3$) was dissolved in 100ml methanol. In the reaction. 1ml of this solution would be equal to $3.8 * 10^{-6}$moles.



Triphenylphosphine

vii) 0.1g $PPh_3=O$ was dissolved in 100ml acetone. 1ml of this solution in the reaction would be equal to $3.6 * 10^{-6}$moles.



$\mathrm{Ph_3P=O}$

Triphenylphosphine Oxide

### 6.1.4 Reaction of Neutramag with industrial sample (1).

As shown in the table below, 20ml of Neutramag was reacted with 10ml of the waste in about 500ml of water (as before) and the resulting solution was made up to 1000ml. The atomic absorption readings were taken on these 1000ml samples and were not diluted further.

The normal standards for discharge into rivers is usually under 10ppm for most metals so for these reactions the idea was to get the metal concentration under 0.1ppm as it was 100 times more dilute than the original.

With hindsight this was a very tough proposition as the scope for error is quite large at such low concentrations and 0.01ppm is quite significant. Apart from this, though, the results did show differences according to ligand; the most significant of these were the results given when the $PPh_3$ was added. (Table 6.1)

**Table 6.1**

| Initial pH | 3.12 | 3.19 | 3.20 | 3.00 | 3.05 | 2.98 |
|---|---|---|---|---|---|---|
| Final pH | 9.13 | 9.13 | 9.45 | 9.45 | 9.51 | 9.52 |
| Ligand added | NONE | $NH_4^+$ | TMEDA | 2*TMEDA | 0.5*TMEDA | bipy |
| Temperature of ligand added (°C) | N/A | 70 | 73 | 72 | 76 | 73 |
| Time (minutes) | 30 | 60 | 60 | 60 | 60 | 60 |
| ppm Ni | 0.20 | 0.08 | 0.10 | 0.06 | 0.03 | 0.08 |
| ppm Cu | 0.13 | 0.12 | 0.06 | 0.21 | 0.13 | 0.13 |
| ppm Zn | 0.07 | 0.05 | 0.04 | 0.06 | 0.05 | 0.05 |
| ppm Fe | 0.39 | 0.37 | 0.12 | 0.32 | 0.31 | 0.35 |
| ppm Pb | 0.03 | 0.04 | 0.03 | 0.02 | 0.02 | 0.03 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Initial pH | 3.03 | 3.02 | 3.02 | 3.03 | 3.03 | 2.96 |
| Final pH | 9.58 | 9.50 | 9.47 | 9.43 | 9.48 | 9.51 |
| Ligand added | phen | $Et_3N$ | $PPh_3$ | $PPh_3$ | $0.5*PPh_3$ | $PPh_3{=}O$ |
| Temperature of ligand added (°C) | 73 | 74 | 72 | room temp | room temp | room temp |
| Time (minutes) | 60 | 40 | 55 | 60 | 60 | 48 |
| ppm Ni | 0.07 | 0.03 | 0.09 | 0.04 | 0.04 | 0.05 |
| ppm Cu | 0.25 | 0.05 | 0.03 | 0.03 | 0.03 | 0.11 |
| ppm Zn | 0.09 | 0.03 | 0.05 | 0.04 | 0.04 | 0.06 |
| ppm Fe | 0.55 | 0.12 | 0.08 | 0.08 | 0.08 | 0.27 |
| ppm Pb | 0.04 | 0.02 | 0.02 | 0.03 | 0.04 | 0.08 |

### 6.1.5 Results

As can be seen from the table the $PPh_3$ was by far and away the best ligand. This parallels the general spectrochemical series of donor atoms $S < O < N < P$, and supports the hypothesis that the stronger the ligand the more effect it will have on the reaction.

### 6.1.6 The apparent oxidation of the iron (II) in the solution

A more significant point to arise from these reactions is that all the iron(II) in the solution, when precipitated, had been oxidised to iron(III); the precipitate was orange/brown and not green. It is accepted that the introduction of ligands into a solution changes the electrode potential of that solution. Unfortunately there are very few methods of showing this; one such method is cyclic voltametry.

However, when more concentrated reactions were performed, it was found that the precipitate was dark green and that the precipitated hydroxide was that of iron (II) and not iron (III). Oxidation may have a profound effect on the concentrated reaction but it is not visually obvious. It would be very difficult to determine the relative amounts of iron (II) and iron (III) in the precipitate, as dissolution of the precipitate in acid would change the balance and some of the iron (II) would be oxidised, thus making the final analysis inaccurate. (There is also no recognised quantitative test for either ferrous or ferric hydroxide when they are present together.)

### 6.1.7 Concentrated reaction.

Reaction was then carried out on a large scale using the original solution of the waste. The concentration of the Neutramag used was 0.32M. The waste was 100 times more concentrated than the solution used in the previous experiments, therefore the concentration of $M^{2+}$ in the solution was $1.65 * 10^{-2}$M

1000ml of the waste solution (~$1.65 * 10^{-2}$ moles) was placed in a beaker. The pH of the solution was pH = 1.32. This is equal to 0.048 moles $H_3O^+$. Thus 0.024 moles of Neutramag was needed to neutralise the acid.

Moles Neutramag needed to neutralise acid = 0.024

Moles Neutramag needed to remove metals from solution = $1.65 * 10^{-2}$

Therefore overall number of moles needed = 0.0405

**Table 6.2**

| Amount of sample added (ml) | Amount of Neutramag added (ml) | Amount of $PPh_3$ added (ml) | Initial pH of the solution | Final pH of the solution | Time (mins) | Excess of Neutramag added |
|---|---|---|---|---|---|---|
| 1000 | 140 | 40 | 1.32 | 9.04 | 40 | 1.2 : 1 |

As can be seen from Table 6.3 the reaction was complete and almost all the metal ions were removed from solution, (all are well below discharge limits). Subsequently Redland has managed to make the reaction work without the addition of $PPh_3$, although they used aeration (described later).

**Table 6.3**

| Metal ion in solution | Initial conc. (mg/l) | Final conc. (mg/l) |
|---|---|---|
| | | |
| $Ni^{2+}$ | 38 | 0.14 |
| $Cu^{2+}$ | 177 | 1.04 |
| $Zn^{2+}$ | 89 | 0.03 |
| $Fe^{2+}$ | 648 | 0.10 |
| $Pb^{2+}$ | 17 | 0.26 |

## 6.2 Industrial waste sample (2)

The second sample that Redland had trouble with was a concentrated solution of titanium and iron (II). Unfortunately there was very little of this solution to do sample reactions on so the solution was diluted 6 times. (Redland still had problems with the dilute solution).

As described previously (2.3), titanium is a very difficult metal to detect accurately on the Atomic Absorption machine due to interferences from other metals present in the solution, and as such only an approximate value for the concentration of the metal ion in the solution was possible. Using the machine as accurately as possible, measuring the concentration of the metals present in a diluted solution (described below), it was only possible to get the concentration to within 10%. So the value of 500ppm ( 0.01M) was taken and was probably a slight over-estimation, how much is arguable. The concentration of the iron (II) however was much larger and thus more significant; that was measured as 2525ppm (0.045M).

170ml of the original solution was made up to 1000ml (6 : 1 dilution) and in this solution, the concentration of $M^{2+}$ was therefore equal to 0.045 moles. Titanium has a normal oxidation state of four ($Ti^{4+}$), thus requiring twice as much Neutramag to precipitate out the hydroxide. The concentration of $M^{4+}$ was 0.010 moles. The pH of the solution was equal to pH = 1.51 which is equal to 0.03 moles of $H_3O^+$. (That requires 0.015 moles of Neutramag to neutralise it.)

(No reactions were actually done on the original solution that Redland provided because there simply was not very much of it and most of it was used up during the more dilute reactions)

| | |
|---|---|
| Amount of Neutramag required to neutralise acid | = 0.015 moles |
| Amount of Neutramag required to remove metals from solution | = 0.065 moles |
| Therefore overall amount of Neutramag needed in the reaction | = 0.080 moles |

The concentration of the Neutramag used was 0.41M. 250ml of this solution was used in the reaction; this was equal to 0.1025 moles of the magnesium hydroxide, which is an approximately 1 : 1.3 ratio of metal ions to Neutramag.

To the reaction was also added 200ml of the $PPh_3$ solution ($7.6 * 10^{-4}$ moles)

### 6.2.1 Results.

As there was very little of the solution to utilise, this was the only reaction done on this sample. The results shown below (Table 6.4) show that although the reaction was very slow eventually all the iron was removed from the solution. Redland did not report that there was a problem with the precipitation of titanium, and our tests on the final solution were only accurate enough to say that the level of titanium was too low to record (less than 5ppm).

**Table 6.4**

| pH of solution | 1.57 | 6.85 | 7.23 | 7.93 | 8.28 |
|---|---|---|---|---|---|
| temperature of reaction (°C) | 20.4 | 22.1 | 23.2 | 23.9 | 24.2 |
| time (mins) | 0 | 60 | 95 | 155 | 435 |

Percentage removal Fe = >99.9 %

Percentage removal Ti = approx. 99%

## 6.3 Industrial waste sample (3)

The third sample that was provided by the company was very concentrated in nickel. As with previous experiments the initial plan with this sample was to start with a comparatively dilute sample of the original and make the solutions more concentrated as each sample is successfully "cleaned up". The original solution was diluted 6 times, as with sample (2).

The concentration of the original solution = 5000ppm in $Ni^{2+}$.

The concentration of Neutramag used = 0.41M.

10ml of the diluted sample was added to approximately 500ml of water in a beaker and the solution stirred. To this was added 40ml of the Neutramag solution and 1ml of the $PPh_3$ solution used in the previous experiment. The initial pH of the solution was pH = 1.60 and as such, extra Neutramag had to be added to compensate for the neutralisation of the acid..

NB. This reaction was too dilute really, as the amount of Neutramag added to the solution to neutralise the acid was much larger than the amount needed to precipitate the metal.

Amount required to precipitate metal = $8.5 * 10^{-4}$ moles

Amount required to neutralise acid = 0.013 moles

### 6.3.1 Results

The nickel was removed to a large extent (final ppm Ni = 0.17). However, because there was a large amount of Neutramag added to neutralise the acid, a small excess in the overall volume would be equal to quite an excess, compared to the amount required to remove the metal ions in the solution. (Table 6.5)

**Table 6.5**

| pH of solution | 1.65 | 7.41 | 8.43 | 9.33 | 9.40 |
|---|---|---|---|---|---|
| temperature of reaction (°C) | 21.3 | 21.4 | 22.6 | 22.7 | 22.8 |
| time (mins) | 0 | 4 | 27 | 78 | 86 |

Percentage removal Ni = >99%

### 6.3.2 Reactions using more concentrated solutions.

As with the previous sample there was not much of this waste to work with; although there were a number of reactions performed using more concentrated solutions, one was never actually done on the concentrated solution itself. As the reactions became more concentrated in nickel then the excess addition of Neutramag became smaller. (If only 1ml is needed to remove the metal ions from the solution and 39 ml are needed to remove all the acid then a 1ml inaccuracy can be a two-fold excess. If on the other hand, 20ml is needed to remove the metal ions from the solution the 1ml is only a small excess in comparison.).

Instead of the previous addition of 10ml of the diluted sample, 100ml and 250ml were added in separate reactions. This was still more than 20 times less concentrated than the original solution. The reaction was performed in a 2000ml beaker and the initial solution was made up to 1000ml before the addition of the Neutramag. (Table 6.6)

A more concentrated Neutramag solution was made up, 1.06M.

**Table 6.6**

| Amount of diluted sample added (ml) | Amount of Neutramag added (ml) | Amount of $PPh_3$ added (ml) | Initial pH of the solution | Final pH of the solution | Time (hours) | Final ppm Ni |
|---|---|---|---|---|---|---|
| 100 | 105 | 120 | 0.77 | 8.89 | 5 | 1.18 |
| 250 | 170 | 200 | 0.52 | 8.26 | 6 | >10 |
| 250 | 170 | 200(*) | 0.52 | 8.64 | 9 | 1.10 |

(*) 0.01 moles of ammonium nitrate was added with the $PPh_3$ to see whether or not the reaction would work better with more than one ligand present. It is difficult to show whether or not the ammonium nitrate made a significant difference as the final pH of the two solutions was very different.

It also shows that the pH required to remove enough nickel ions to achieve a successful reaction is greater than pH 8.3

### 6.4 Industrial waste sample (4)

This sample was the most concentrated of the ones tried so far. It happened to be concentrated in the two worst elements for Redland, iron (II) and nickel. The solution was also very acidic and stronger Neutramag slurry was prepared. As described previously (2.2) the Neutramag itself is too viscous to stir in the lab, so a slurry was made up as concentrated as possible (in this case 1.06M). (The original slurries are approximately 8M).

The concentration of metals in the original solution was as follows,

ppm Zn = 41
ppm Fe = 14650
ppm Ni = 1775
ppm Cr = 15

This was equal to a metal concentration of 0.293M .

### 6.4.1 Initial reactions.

pH of the solution = 0.32
Moles of $H_3O^+$ = 0.48
1000ml of the sample = 0.293 moles $M^{2+}$ + $M^{3+}$ ($Cr^{3+}$)
Amount of Neutramag required = 0.54 moles

1000ml of the sample was placed in a large container (half a bucket). To this was added 570ml of the 1.06M Neutramag and 20ml of the $PPh_3$ solution. 570ml is equal to a 1: 1.3 excess of magnesium hydroxide.

The solution was left to react for two and a half days and only then was the concentration of the iron below 10ppm. So a reaction on a more dilute scale was tried.

### 6.4.2 Dilute reaction.

250ml of the sample was made up to 1000ml with water. To this solution 10ml of the $PPh_3$ solution was added and the mixture was stirred for 25 mins. The idea of adding the ligand first was to try and get as much of it complexed as possible before the Neutramag was added and hopefully to speed up the reaction (see Table 6.7). This was successful and so the same reaction was attempted using a neat solution of 1000ml. This however was very slow (see below).

Table 6.7

| Amount of sample used (ml) | Amount of Neutramag added (ml) | Amount of $PPh_3$ added (ml) | Initial pH of solution | Final pH of solution | ppm Zn | ppm Fe | ppm Ni | ppm Cr |
|---|---|---|---|---|---|---|---|---|
| 250 | 150 | 15 | 0.74 | 9.27 | 0.13 | 1.59 | 0.19 | 0.09 |
| 1000 | 600 | 50 | 0.85 | 8.76 | N/A | 0.22 | N/A | N/A |

Time taken for the first reaction was 5 $^1/_2$ hours.

Time taken for the second reaction was 2 $^1/_2$ days.

### 6.4.3 Stage process.

When the concentration of the reaction is doubled the time increases four fold. There must be something else which is important in the reaction. A stage process was tried where the precipitate was removed periodically by filtering and the solution left to react.

This was achieved by adding aliquots of Neutramag separately and not adding the whole amount in one. The reaction was left to equilibrate and the precipitate removed. This method still achieved the same result as previously, although it took much longer in the lab and it was not possible to say whether or not it would work on an industrial scale.

## 6.5 Generic waste.

Because there were not sufficient quantities of the waste provided by Redland, it was decided that the easiest way around the problem was to make a solution of similar metal concentration to one of the samples provided. The one that was chosen to be copied was industrial sample 4 as the triphenylphosphine seemed to have a more pronounced effect on iron (II) than any of the other metals.

### 6.5.1 Generic waste (1)

The concentration of metals in the solution was made up as follows;

ppm Fe = 14,200
ppm Ni = 1,760
ppm Zn = 360

This is equal to an overall metal concentration of 0.290M.

A new sample of Neutramag was diluted down and the concentration was determined to be 2.7M. A new sample of $PPh_3$ was prepared. 1g $PPh_3$ was dissolved in 250ml of acetone, thus 1ml of this solution would contain $1.5 * 10^{-5}$ moles $PPh_3$. This figure was totally arbitrary.

250 ml of the generic sample was made up to 1000 ml in water. To this was added 50ml of the Neutramag slurry along with 10ml of the $PPh_3$ solution. The reaction was repeated with the addition of air being bubbled through the solution from a glass pipette. The idea behind this was to try and help oxidise some more of the iron (II) to iron (III) and speed up the reaction. It is a ploy that Redland uses in industrial applications, with which they have had limited success.

An excess of Neutramag was needed to complete the reaction; a preliminary experiment with 40 ml of Neutramag was insufficient to drive the reaction to completion. Although there is an excess, with just adding 40ml, it does not appear to work. As was discussed previously (6.1.6) it is suspected that some of the iron (II) in the reaction will be oxidised to iron (III). Although that absolute value is not known, more Neutramag is need to precipitate iron (III) than iron (II). This could be an explanation of why a larger excess is required than one would think necessary.

**Table 6.8**

| Amount of diluted sample added (ml) | Amount of Neutramag added (ml) | Amount of $PPh_3$ added (ml) | Initial pH of the solution | Final pH of the solution | Time (mins) | Excess of Neutramag added |
|---|---|---|---|---|---|---|
| 250 | 50 | 10 | 1.60 | 8.80 | 160 | 1.6 : 1 |
| 250 | 50 (*) | 10 | 1.74 | 8.92 | 60 | 1.5 : 1 |

(*) With aeration (bubbling through of compressed air)

In both samples the concentration of all three metals present was below 0.2ppm and as such, safely within discharge limits.

As can be seen from the above results (Table 6.8), the bubbling of compressed air through the solution has a pronounced effect on the reaction. This may not necessarily just be due to the oxidation of some of the iron (II) to iron (III). The reaction may also be aided in some way by the bubbles themselves, for example by increasing the surface area of contact between the Neutramag and the metal solution, thus creating a region in which reaction is more favourable, (slightly increased pressure and more excitation).

It might be possible to demonstrate the existence of such an effect by bubbling nitrogen through the reaction instead of compressed air. This contains no oxygen and should not aid the oxidation of the iron (II) to iron (III).

It was decided to bubble air through all the reactions from now on, just so that the reaction was made faster and thus more reactions could be done in the limited time. None of the reactions have been done without the addition of compressed air, to compare times, as this was considered to be a waste of the available time.

### 6.5.2 Generic waste (2)

Another sample was made as it was apparent that a large volume of the generic waste would be used in a short period of time and only 1000ml of generic waste (1) was made up.

The concentration of metals in the solution (2) was made up as follows;

ppm Fe = 13,680

ppm Ni = 1,880

ppm Zn = 400

This is equal to an overall metal (all initially $M^{2+}$) concentration of 0.271M.

500ml of the generic sample was made up to 1000ml in water and the volume of Neutramag and $PPh_3$ was doubled as well. As with previous reactions, the reaction took more than double the length of time to complete (Table 6.9).

**Table 6.9**

| Amount of diluted sample added (ml) | Amount of Neutramag added (ml) | Amount of $PPh_3$ added (ml) | Initial pH of the solution | Final pH of the solution | Time (mins) | Excess of Neutramag added |
|---|---|---|---|---|---|---|
| 500 | 120 | 50 | 0.92 | 8.88 | 260 | 1.65 : 1 |

### 6.5.3 Reactions with increasing amounts of added $PPh_3$

Another sample was made up; generic waste (3). The concentrations of the new solutions are shown below. A new solution was made up so the new reactions would all be performed on the same solution.

ppm Fe = 13,520
ppm Ni = 1,680
ppm Zn = 1,120

This is equal to an overall metal concentration of 0.288M.

A new Neutramag slurry was made up and the concentration of magnesium hydroxide was calculated at 3.42M.

As discussed in the previous section, when the $PPh_3$ solution is added to the reaction mixture, a white solid is seen to appear on the surface of the solution. This is because $PPh_3$ is insoluble in water. The addition in this series of reactions of larger and larger quantities of the $PPh_3$ solution only compounds this problem.

One must assume that because it is so insoluble, the most probable mechanism for reaction between the ligand and the metal ions is direct reaction of the aquo-complex with the solid.

$$M(H_2O)_6^{2+} + PPh_{3(s)} \longrightarrow [M(H_2O)_5PPh_3]^{2+} + H_2O$$

Thus with a larger addition of the solution to the reaction, in essence the surface area of solid $PPh_3$ to react with the metal ions in the solution is increased. If the $PPh_3$ could somehow be distributed more homogeniously in the solution then it would probably react even faster.

As can be seen from the table below (Table 6.10), the addition of more $PPh_3$ to the reaction does in fact increase the rate. The absolute number of moles of $PPh_3$ added to the reaction, however, should not be taken at face value, as a large percentage of this does not actually react with the metal ions and just gets filtered off at the end of the reaction.

FOOTNOTE

This phenomenon, incidentally, may also be to the advantage of industry. Because of tight restrictions on discharge levels of phosphorus-containing compounds, i.e. phosphate fertilisers etc., only a small amount of the $PPh_3$ would be allowed to be discharged. Since $PPh_3$ is not soluble in water, it can also be assumed, unless the ligand is actually bonded to the metal ions left in the final solution, on discharge, that any excess of the $PPh_3$ would be filtered off with the solid hydroxides at the end of the reaction.

The amount of metal ions left in the final solution is almost always below 0.5ppm. At the beginning of the reaction the ratio of $PPh_3$ to metal ions is less than 1 : 500 in most cases. However when the reaction is finished the ratio of $PPh_3$ to metal ion present is greater than 20000 : 1. So one must assume that because the $PPh_3$ is not soluble in water, it does not react in a large enough quantity to hold the metals in solution.

It can reasonably be assumed that no more than six $PPh_3$ molecules can be attached to one metal, so that for a given metal concentration of 0.5ppm, for example on discharge, the maximum concentration of $PPh_3$ that may be discharged in this way would only be 3ppm.

Unfortunately no literature has been found concerning work with $PPh_3$ in aqueous solution, which is understandable as the chemistry is rather limited by the insolubility. A better understanding of the chemistry of $PPh_3$ complexes would require much more experimental work, beyond the time limitations of the present project.

**Table 6.10**

| Amount of diluted sample added (ml) | Amount of Neutramag added (ml) | Amount of $PPh_3$ added (moles) | Initial pH of the solution | Final pH of the solution | Time (mins) | Ratio of $PPh_3$ added vs. metal conc. |
|---|---|---|---|---|---|---|
| 250 | 50 | $6.1*10^{-4}$ | 1.33 | 8.60 | 140 | 1 : 230 |
| 250 | 50 | $1.2*10^{-3}$ | 1.57 | 9.06 | 125 | 1 : 120 |
| 250 | 50 | $1.8*10^{-3}$ | 1.20 | 8.75 | 73 | 1 : 80 |
| 250 | 50 | $2.4*10^{-3}$ | 1.43 | 8.75 | 75 | 1 : 60 |

The concentrations of the 3 metals in each of the final solutions was below 0.5ppm

The table above also shows that after a point (approximate ration of 1 : 80) the amount of $PPh_3$ added does not affect the reaction. This is probably due to the fact that there is an upper limit on how fast the metal aquo-complexes will react with the solid $PPh_3$.

### 6.6 Possible methods of addition of $PPh_3$ into the reaction.

$PPh_3$ itself is insoluble in water. However if a species containing $PPh_3$ could be added to the solution and then somehow released into the reaction, the addition of the $PPh_3$ to the metal ions may be faster and thus speed up the reaction. It would be advantageous to avoid the addition of organic solvents to the reaction.

If $PPh_3$ is added to conc. sulphuric acid the phosphorus is protonated and the solid dissolves to form the salt $HPPh_3^+HSO_4^-$. This can be shown to exist using NMR. As can be seen from the NMR spectra shown below , $PPh_3$ itself (in acetone here) shows one peak in the $^{31}P$ spectrum, ($\delta$ = -4.68ppm) (Spectrum1),whereas the $HPPh_3^+$ shows a doublet in the $^{31}P$ spectrum ($\delta$ = 7.45 ppm, $^1J_{PH}$ = 500.3Hz). (Spectrum 2) (lit. $\delta^{31}P$(liq. HCl) = 6.0ppm, $^1J_{PH}$ =512 ±5Hz) [10].

Unfortunately when this solution is added to a less acidic solution (pH < 1) the salt breaks down and the $PPh_3$ is seen to precipitate out. This is not necessarily a bad thing as it introduces the $PPh_3$ as a very fine precipitate and not as large crystals. No further work was attempted using this method, however, due to time constraints.

## 6.7 Possible mechanisms for the reaction of Neutramag with the ligand complexes

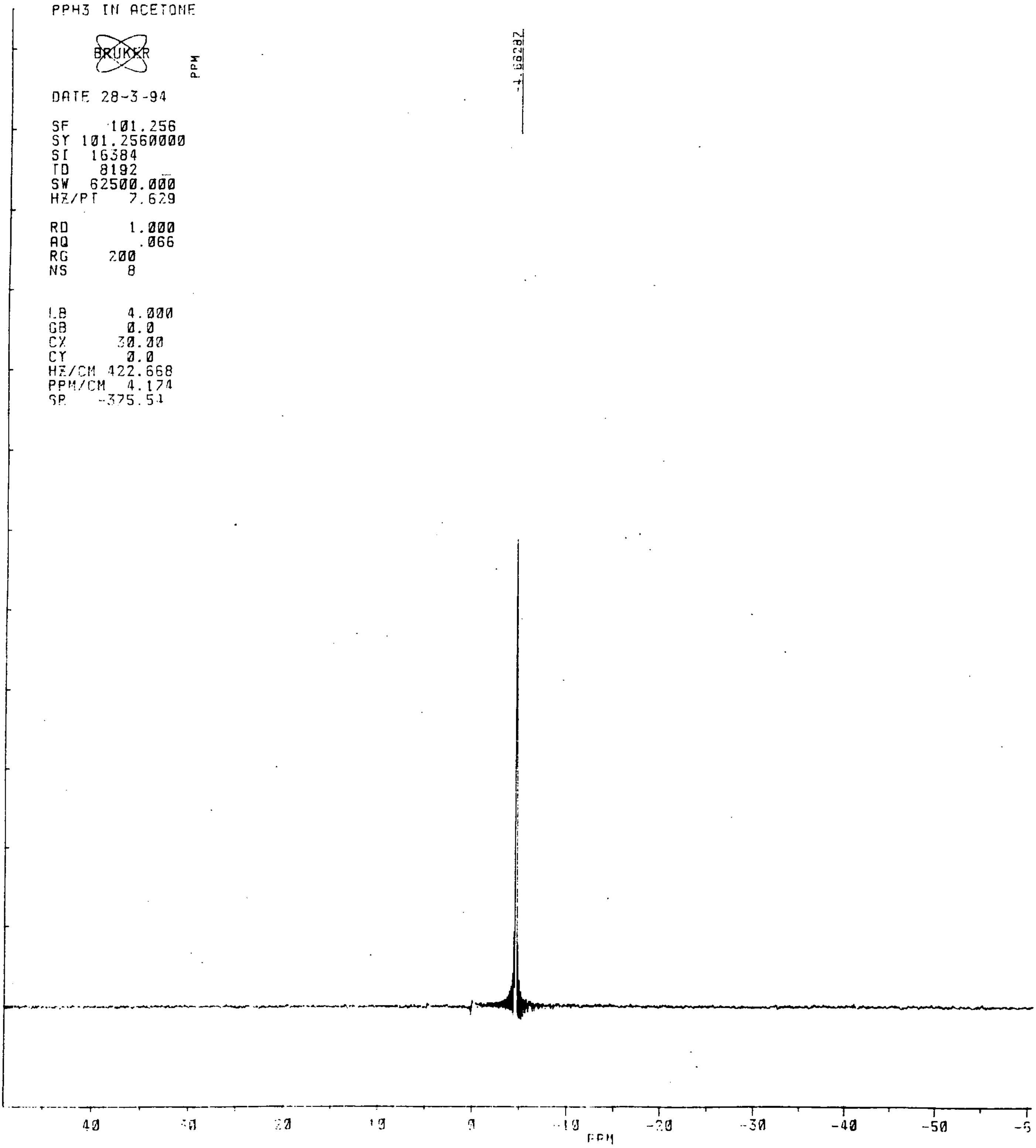
The existence of compounds containing $M^{2+}$ ions and $PPh_3$ has been widely reported e.g. $FeCl_2(PPh_3)_2$[11], $NiCl_2(PPh_3)_2$[12]. Knowing that these exist it is reasonable to assume that $PPh_3$ will complex with the transition metals present in the reactions. Although there are no references in the literature, probably due to the insolubility of $PPh_3$ in an aqueous solution, one must assume that complex formation is possible for an understanding of the mechanism to be attempted.

In the solution the metal ions are present most commonly as the hexa-aquo complexes e.g. $[Fe(H_2O)_6]^{2+}$. When precipitation of the hydroxide occurs the mechanism does not involve substitution of one of the water molecules for a hydroxide ion, rather the removal of a proton from one of the waters already on the metal.[13]

In each of the four mechanisms listed here, the metal and the charge on the complex have been left out so that they can be used for more than one metal. (All complexes are assumed to be for a doubly charged cation ($M^{2+}$) i.e. the maximum number of hydroxide ions that can be added is two).

# Spectrum 1

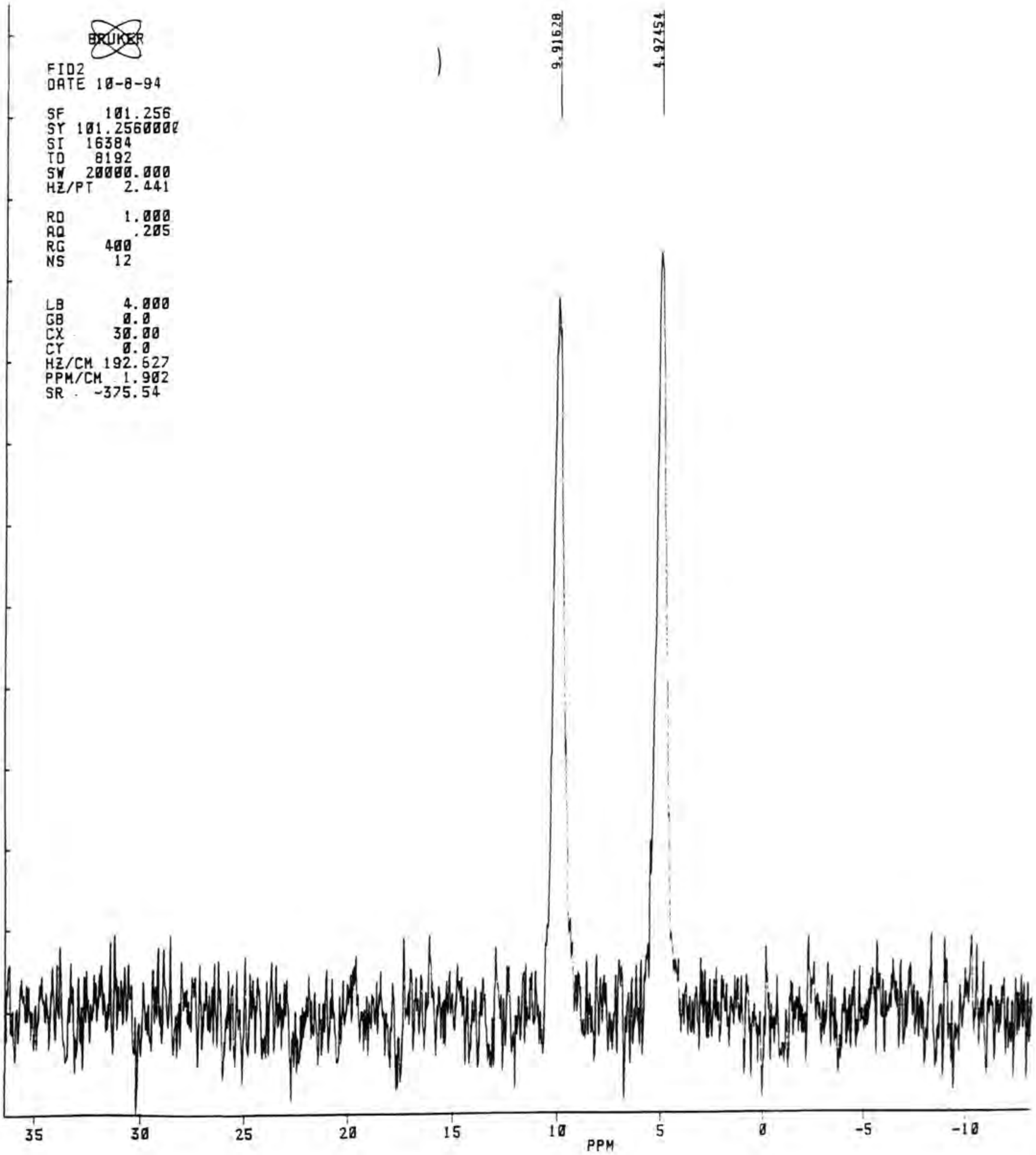
## $^{31}$P spectrum of $PPh_3$ in acetone



```
PPH3 IN ACETONE

BRUKER

DATE 28-3-94

SF     101.256
SY 101.2560000
SI   16384
TD    8192
SW  62500.000
HZ/PT    7.629

RD        1.000
AQ         .066
RG      200
NS        8

LB        4.000
GB        0.0
CX       30.00
CY        0.0
HZ/CM 422.668
PPM/CM   4.174
SR    -375.54
```

## Spectrum 2

### $^{31}$P spectrum of $^{+}$HPPh$_3$ in conc. sulphuric acid



## Mechanism 1

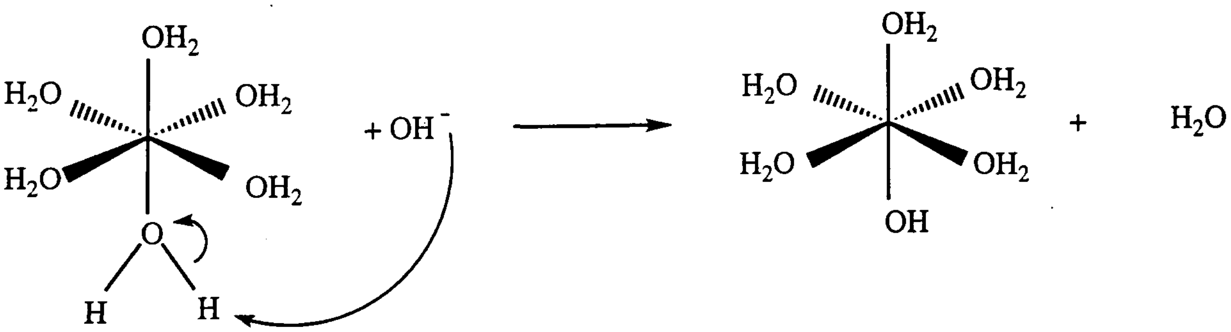
The initial stage in any precipitation by hydroxide is not substitution of water, but the abstraction of a proton from one of the water molecules. An analogous system is in the base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ where the abstraction of a proton from an $NH_3$ group is the first step in the mechanism.[12]

$$[Co(NH_3)_5Cl]^{2+} + OH^- \overset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4NH_2Cl]^{+} + H_2O$$

$$[Co(NH_3)_4NH_2Cl]^{+} \xrightarrow{\text{slow}} [Co(NH_3)_4NH_2]^{2+} + Cl^-$$

$$[Co(NH_3)_4NH_2]^{2+} \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{2+}$$

## Mechanism 1

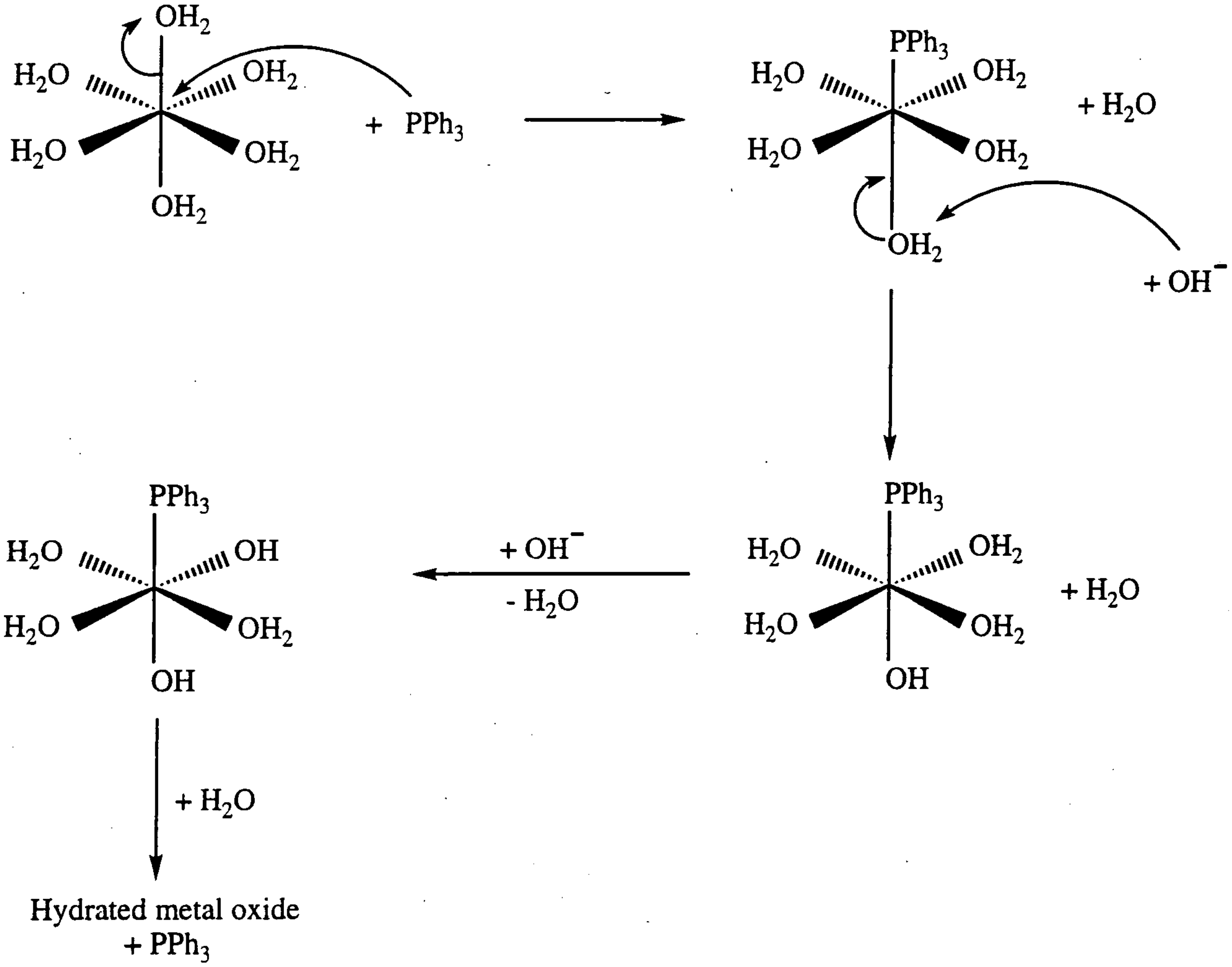


## Mechanism 2

If we assume that the ligand (in this case $PPh_3$) substitutes a water molecule in the hexa-aquo complex, we can also make the assumption that the bond formed between the $PPh_3$ and the metal in question will be stronger, and thus shorter, than the respective bond between the metal and the remaining water molecules.

Because the P-Metal bond is stronger, it may affect the bond between the metal and the water trans to the $PPh_3$, causing it to be weaker and longer. If this is so, then the abstraction of a proton from the water in question is more probable than before. The $PPh_3$ may then be released on precipitation of the hydrated metal oxide, thus accounting for its catalytic properties.

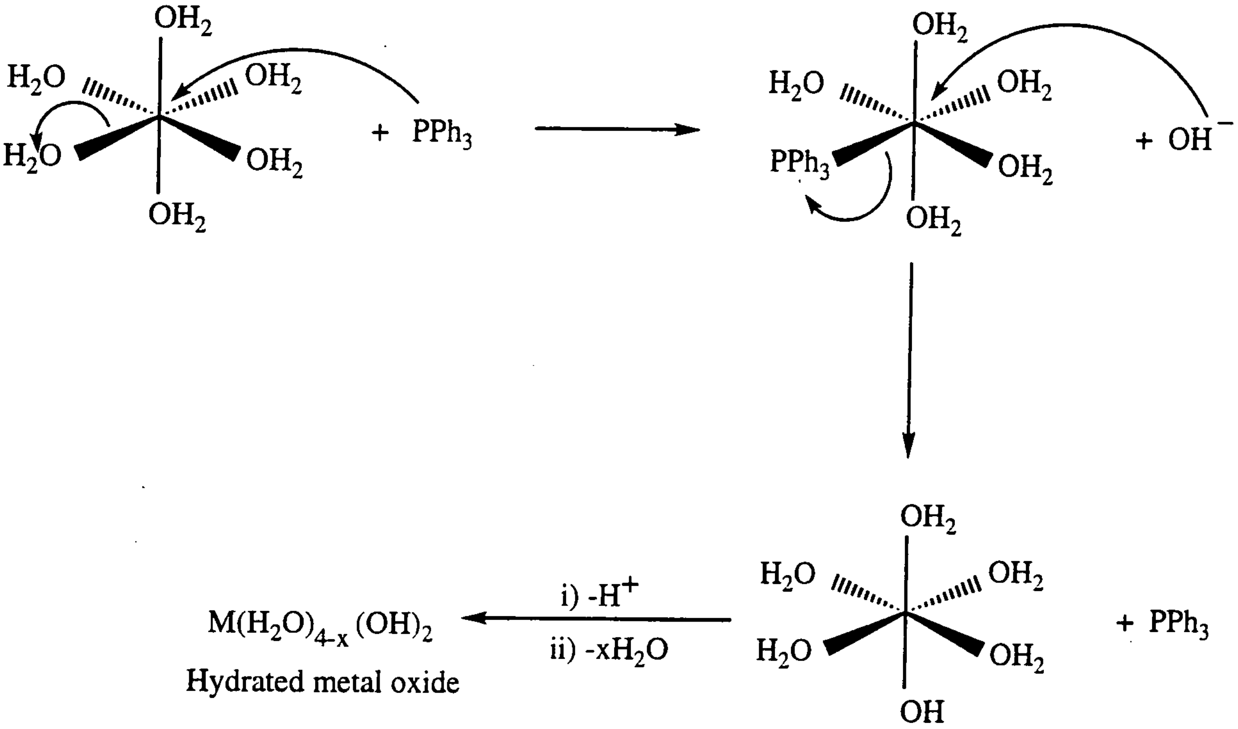
**Mechanism 2**



## Mechanism 3

Again, assuming that the $PPh_3$ substitutes for a water molecule in the complex, there would now be the possibility of direct substitution of the $PPh_3$ by an $OH^-$ ion. Whether or not this is more probable than proton abstraction is debatable and impossible to measure with simple experiments. However, this may provide an explanation of how the $PPh_3$ is removed from the complex (see Mechanism 4)

### Mechanism 3



## Mechanism 4

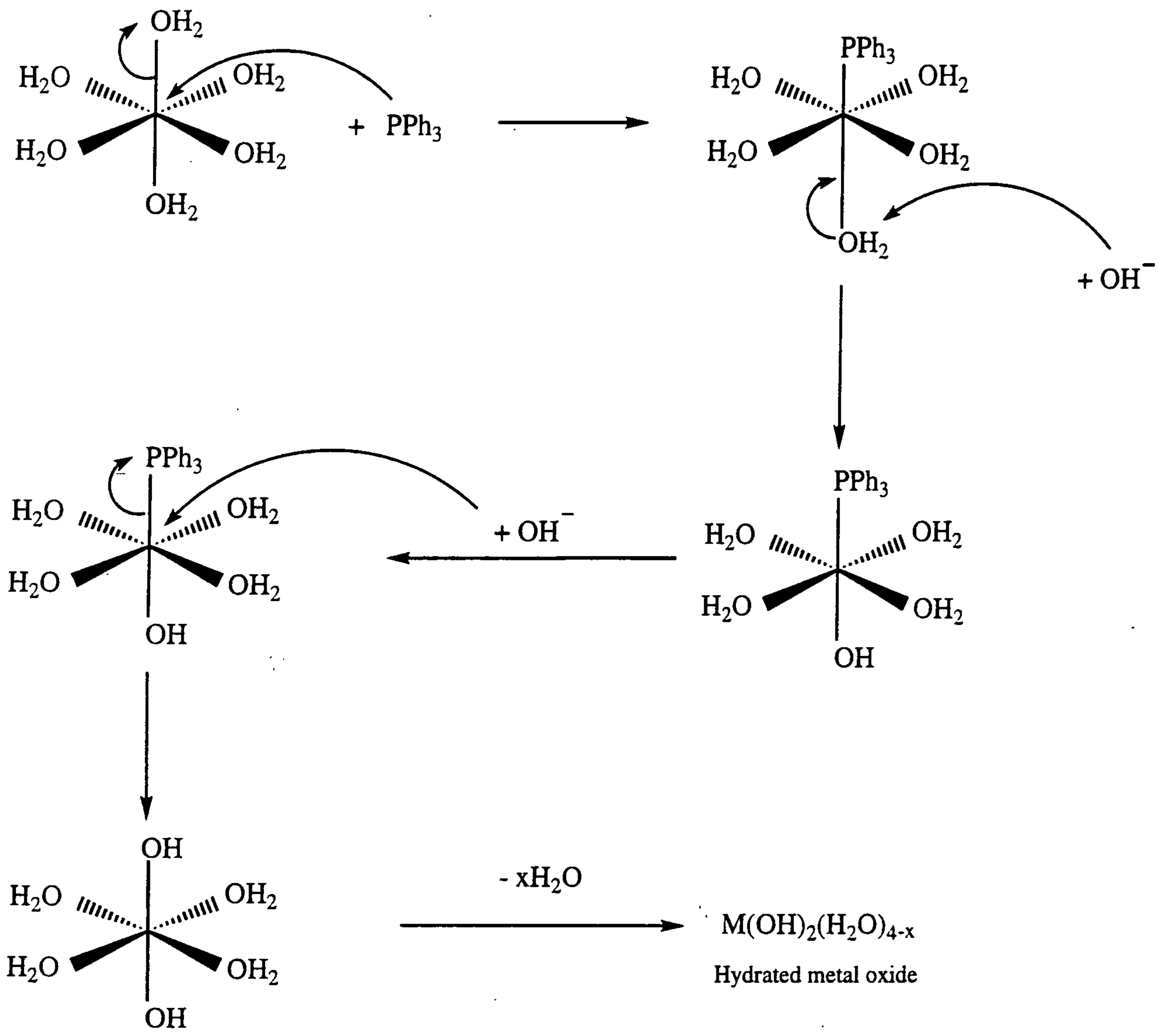
It has already been established, in this work, that the role of the ligand ($PPh_3$) is catalytic. This is because it is added in small quantities and if it were not then the reaction would grind to a halt very quickly. If the ligand is to have a catalytic effect then as well as complexing with the metal in the first place, it must also be removed from the complex when it has had the desired effect.

If we are assuming that in the first instance the ligand substitutes for a water molecule in the aquo complex, then it is unlikely that the final step in the mechanism is going to be substitution of the $PPh_3$ by a water molecule (mechanism 2). This only leaves one of two possibilities; either the $PPh_3$ migrates from the molecule and water substitutes via an $S_N1$ type mechanism, or more likely, a hydroxide ion substitutes for the $PPh_3$.

This presents a problem in itself. If we are going to assume that there is substitution of the ligand by hydroxide ions, can we predict whether or not it will be more favourable than proton extraction as either the first step in the mechanism, the second or indeed the third step?

In the mechanisms above the charges on the complexes have been ignored. However if we take this into account (for example for an $M^{2+}$), once there has been incorporation of a hydroxide into the complex, whatever the mechanism, the charge on that complex will decrease. Because the charge on the complex has decreased, and there is one less water molecule to abstract a proton from, the complex itself is less "acidic". Thus there is a smaller probability that a hydroxide ion will abstract a proton from the complex. This will therefore increase the probability that there will be substitution of the $PPh_3$ by a hydroxide ion (probably via an $S_N2$ reaction) (Mechanism 4).

# Mechanism 4


OH2
H2O
OH2
H2O
OH2
OH2
+ PPh3
PPh3
H2O
OH2
H2O
OH2
OH2
+ OH⁻
PPh3
H2O
OH2
H2O
OH2
OH
+ OH⁻
PPh3
H2O
OH2
H2O
OH2
OH
OH
H2O
OH2
H2O
OH2
OH
- xH2O
M(OH)2(H2O)4-x
Hydrated metal oxide

The decrease in charge of the complex will decrease the electrostatic attraction between the new intermediate complex and another hydroxide ion in solution. This, however, is overcome due to the insolubility of the metal hydroxide. Complexation of any metal by ligands has formation constants for each step of the reaction ($K_n$). The step constants for the reaction, electrostatically and statistically, normally decrease i.e. $K_1 > K_2 > K_3$ etc., meaning it is harder to complex a second ligand than the first.

$K_n$ = step formation (equilibrium) constant for the reaction $ML_{n-1} + L \rightleftharpoons ML_n$

The overall reaction constant, β, is the product of all the step constants (see over page). For magnesium hydroxide this is also the reciprocal of the solubility product. Thus in these reactions $K_2$ will actually be larger than $K_1$ due to the large lattice energy of the solid hydroxide and its insolubility. (see 6.8)

$\beta_n$ = overall formation constant for the reaction $M + nL \rightleftharpoons ML_n$

## 6.8 Determination of $K_1$ and $K_2$

$K_1$ = formation constant for addition of hydroxide ion to metal (whether it is by proton abstraction or substitution)

$$M^{2+} + OH^- \rightleftharpoons [M(OH)]^+$$

$$K_1 = \frac{[M(OH)^+]}{[M^{2+}][OH^-]}$$

$K_2$ = the formation constant for the addition of a second hydroxide ion to the complex.

$$[M(OH)]^+ + OH^- \rightleftharpoons [M(OH)_2]$$

$$K_2 = \frac{[M(OH)_2]}{[M(OH)^+][OH^-]}$$

$$[M(OH)^+] = K_1[M^{2+}][OH^-]$$

Substituting for $[M(OH)]^+$

$$K_2 = \frac{[M(OH)_2]}{K_1[M^{2+}][OH^-]^2}$$

$$K_1K_2 = \frac{[M(OH)_2]}{[M^{2+}][OH^-]^2} = \beta_2$$

$$\beta_2 = \frac{1}{K_{sp}}$$

(since $[M(OH)_2]$ may be taken as negligible, for a sparingly soluble solid)

**Table 6.11**

| Metal | $\log_{10}K_1$ [15] | $\log_{10}K_2$ |
|---|---|---|
| $Fe^{2+}$ | 6.10 | 9.00 |
| $Ni^{2+}$ | 4.70 | 12.48 |
| $Zn^{2+}$ | 5.77 | 10.92 |

$K_2$ values are calculated from the equation:

$$K_1K_2 = \beta_2 = \frac{1}{K_{sp}}$$

As can be seen from Table 6.11 assume that the concentration of magnesium hydroxide in solution is negligible and constant, values can be calculated for $K_1$ and $K_2$. This shows that in the cases above $K_2 > K_1$ and thus negating the problem due to the lower electrostatic attraction, in comparison with the insolubility of the hydroxide.

# Chapter 7

# Conclusions

## 7.1 Do we understand the reasons for the initial problems?

The initial purpose of the project was to try and understand why some metal hydroxides did not precipitate as readily as expected upon the addition of magnesium hydroxide, sometimes requiring a large stoichiometric excess. Although this is still not fully understood, a better understanding of how to approach the problem has been obtained this year. The problem has been tackled in stages (i.e. via experiments on one or two metals before progressing to mixtures containing several metals, including actual industrial waste samples which had proved difficult to treat). From the outset attempts were made to try and make the reactions work in some way and hopefully then a greater understanding of the original problem could be achieved.

## 7.2 What has been accomplished this year?

The main achievement has been to show that the presence of catalytic quantities of certain ligands, for which triphenylphosphine has so far proved the most suitable, greatly accelerate the deposition of the metal hydroxides. Various hypotheses have been put forward in the thesis to account for this behaviour, and since further work sponsored by Redland is to take place this year, it should be possible to investigate some of these points more thoroughly. The problem mentioned in 7.1 has also been shown to be kinetic rather than thermodynamic in origin, at least in the case of iron (II).

## 7.3 Ideas for further work in the area.

There are a number of areas of the project that have not been investigated fully at due to time constraints. Although there is no guarantee that any of these avenues of investigation will be fruitful, further work in a number of areas seems desirable.

1) The addition of ligands to the reaction mixtures. Triphenylphosphine turned out to be the best ligand in the project, although it should be noted that this was for solutions containing large quantities of iron (II). We believe that this may not be the best ligand for mixtures of solutions. e.g. $NH_3$ may be a better ligand that $PPh_3$ for hard metal ions such as $Ti^{4+}_{(aq)}$. This is because phosphorus is a "softer" ligand than $NH_3$ and is unlikely to bond to the metal quite as well. If this is the case then perhaps a mixture of ligands added to a mixture of metals in solution may give the faster reaction kinetics and the best percentage removal of the metal ions.

2) The use of aeration in the reaction has not been investigated quantitatively. Does the addition of compressed air speed up the reaction because of oxidation of the iron (II) to iron (III), or is it because of some other reason e.g. providing a more favourable reaction condition, due to the bubbles.

3) The mechanism of the process involving ligands is not really understood, and although we can make educated guesses at it, only more kinetic work can give us a true understanding of the reaction mechanism. This may lead to an understanding of the process without the addition of the ligands.

4) Work needs to be carried out into investigating the pH values at which all the metals precipitate. Although this work was started by the pupils of Benet Biscop School in their project week not enough data was produced for inclusion in the thesis. Investigation also needs to be carried out to see whether the pH of precipitation changes with addition of other metal and ligands.

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2ND EDITION

## Board of Studies in Chemistry

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| May 12 | Prof. D. A. Humphreys, McMaster University, Canada<br>Bringing Knowledge to Life | |

* Attended

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