CHAPTER VIII

HYDROLYSIS AND CORROSION OF IRON
IN AQUEOUS AMMONIUM FERROUS SULPHATE SOLUTION

The hydrolysis products, from ferric salt solutions both soluble species and insoluble precipitates, have been extensively studied by a number of investigators, by various experimental methods. The effect of different anions and cations on the hydrolysis of these solutions have also been studied. The effect of ammonium sulphate on the hydrolysis of ferric sulphate has been studied by Maryan'chik and Zapol'skii (1972) using thermogravimetry and X-ray diffractometry. Umetsu et al (1977) have studied the effect of other metal sulphates on the hydrolysis of ferric sulphate solution. Ujihira et al (1978) have studied the effect of the addition of urea on the hydrolysis of $\text{Fe}_2(\text{SO}_4)_3$ solution.

The hydrolysis of ferrous salt solutions are comparatively less studied and very few studies are available on the hydrolysis products from double salts. Sung et al (1975) have studied the formation of $\alpha$-$\text{FeOOH}$ by the hydrolysis of ammonium ferrous sulphate (Mohr's salt) solution at $90 - 100^\circ\text{C}$ with different contents of iron in the solution. This chapter presents the results of an investigation of the hydrolysis products formed from ammonium ferrous sulphate solution under different conditions of temperature, pH and concentration of ammonium.
The RT Mössbauer spectrum of ammonium ferrous sulphate ($\Delta = 1.77$ mm/s, $\delta = 1.08$ mm/s) is shown in Fig. 8.1. Corrosion of iron in ammonium ferrous sulphate solution at RT, 50°C and 80°C have also been analysed here. The results obtained and the inferences drawn from the study of hydrolysis are applied to explain the mechanism of the formation of corrosion products of iron in ammonium ferrous sulphate solution.

8.1. PREPARATION OF SAMPLES

20%, 10% and 1% ammonium ferrous sulphate solutions have been prepared and are allowed to hydrolyse in open atmosphere. The products, at the end of five days are filtered, washed with distilled water, alcohol and acetone, and dried. Some samples have been prepared by bubbling air through the solution for different lengths of time.

The 20% and 10% solutions have been hydrolysed at different pH values in the pH range 3 to 6 at RT. The initial pH has been either increased or decreased by the addition of dilute NH$_4$OH or dilute H$_2$SO$_4$, respectively. The products formed in the solutions with initial pH 3.5, 4.0, 4.5 and 6.0 have been investigated. On increasing the pH to about 5.6 by the addition of alkali (NH$_4$OH), precipitation occurred immediately. The pH has been further raised to 6.0 and the 'immediate precipitates' have been separated
and studied. In another series of experiments, the precipitate formed has been left in the solution and the final products at the end of five days have been filtered out and studied.

Hydrolysis of 20% and 10% solutions have also been carried out at 50°C and at 80°C by keeping the solutions in a constant temperature water bath. The products formed after different periods of time have been separated and studied. The hydrolysis products formed in the boiling solutions have also been investigated.

Corrosion of electrolytic iron powder (see Appendix B for characterisation) in 20% and 10% ammonium ferrous sulphate solution has been carried out in a similar way to that of the corrosion of iron in other ammonium salt solutions described in previous chapters.

8.2. RESULTS AND DISCUSSIONS

8.2.1. Hydrolysis of Ammonium Ferrous Sulphate Solution

The RT hydrolysis product of 20% solution (pH ~ 3.8) is identified to be aminojarosite $\text{NH}_4\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2$ by Mössbauer and X-ray diffraction studies. The Mössbauer spectra of this sample, recorded at RT and 85 K are shown in Fig. 8.2. Both the spectra are doublets indicating that the compound is paramagnetic down to 85 K. A higher line-width (~6.5 mm/sec) at RT as compared to the line-width
at 85°C (∼0.4 mm/sec) is probably due to inhomogeneous broadening. The Mössbauer parameters are listed in table 8-1. The isomer shift values and the quadrupole splitting obtained here are in agreement with those reported from previous Mössbauer effect studies of the Jarosite (Hryniewicz et al., 1965; Takano et al., 1968). A scanning electron micrograph of the jarosite formed in 20% solution is shown in Fig. 8.10a. The isomer shifts of 0.4 mm/sec with respect to α-Fe shows that iron atoms are present in the trivalent state. The quadrupole splitting (1.2 mm/sec) however is too large for hydrated trivalent iron atoms. In amino jarosite iron atoms are present in the Fe(OH)₄(SO₄)₂ octahedra (Hryniewicz et al., 1965; and Wang et al., 1965). Therefore the sulphate ions, bound to Fe (III) ion closely must have a large contribution to the electric field gradient at the ⁵⁷Fe(III) nuclei.

Fig. 8.3 shows the XRD pattern of the sample taken using Mo-Kα radiation. In table 8-2, the d values and the relative intensities of the X-ray diffraction lines obtained for jarosite are listed along with the standard pattern.

The hydrolysis product from 10% solution (pH ∼4.0) comprised of a mixture of about 44% amino jarosite and 56% superparamagnetic (SPM) α-FeOOH (goethite). A 1% solution (pH 4.7) however forms only SPM α-FeOOH. The identification of α-FeOOH is also accomplished by XRD and IR absorption studies. The RT Mössbauer spectra of the hydrolysis products of 20% and 1% solution are shown
in Fig. 8.4. The isomer shift and the quadrupole splitting of the SPM α-FeOOH are typical of ferric oxyhydroxide whose structure is represented by the octahedral Fe (O, OH)₆. The smaller quadrupole splitting (1.0 mm/sec) of the jarosite formed from 10% solution may be expected to be due to the deviation from the stoichiometry.

The infra red absorption spectra of the precipitates from 20% solution and 1% solution are shown in Fig. 8.5. The NH₄⁺ group shows a broad band centred near 3250 cm⁻¹ resulting from NH₄⁺ antisymmetric stretching vibrations and a strong absorption band in the range 1390 - 1430 cm⁻¹ resulting from the NH₄⁺ bending vibration. The H-O-H bending motion is characterised by an absorption band near 1450 cm⁻¹. Strong bands associated with OH stretching vibrations of water and hydroxyl groups occur between 3200 and 3700 cm⁻¹. Sulphates show very strong band in the range 1130 - 1080 cm⁻¹ and considerably weaker band in the region 610 - 680 cm⁻¹. The amino jarosite is characterised by a triplet absorption at 1010 cm⁻¹, 1080 cm⁻¹, and 1210 cm⁻¹ in this region and a weaker one at 450 cm⁻¹. The other key bands are obtained at 505 cm and 475 cm⁻¹. α-FeOOH shows characteristic bands at 800 cm⁻¹ and 900 cm⁻¹ which are potentially used for its identification as has been indicated in previous chapters.

When air is bubbled through the 20% and 10% solutions at RT, formation of a basic iron sulphate
$\text{Fe(OH)}_2\text{SO}_4$ is indicated along with jarosite. Fig. 8.6 shows the Mössbauer spectra of the hydrolysis products formed from 10% solution aerated for five days. The spectrum at 82 K clearly shows a diffuse hyperfine pattern corresponding to an internal field of about 328 kOe, in agreement with the previously reported value for $\text{Fe(OH)}_2\text{SO}_4$ (Rumbold and Wilson, 1974). X-ray diffractograms do not show a clear evidence for the presence of $\text{Fe(OH)}_2\text{SO}_4$ in aerated samples. It could be poorly crystalline and therefore X-ray amorphous. Infra-red absorption spectra, however show that the peaks in the region $1000 \text{ cm}^{-1} - 1200 \text{ cm}^{-1}$ get broadened indicating the presence of a $\text{SO}_4^{2-}$ group having different coordinations than jarosite. An absorption band is also indicated at $655 \text{ cm}^{-1}$. No $\alpha$-FeOOH is found in the precipitate from aerated 10% solution.

A systematic study of the dependence of the species formed in 20% and 10% solution on the pH has also been made here. Figs. 8.7 and 8.8 respectively show the Mössbauer spectra of the hydrolysis products of 20% and 10% solutions with different initial pH values of <3.8, 4.0, 4.5 and 6.0. The results of the analyses of the spectra are listed in table 8-3. The identification of the products are confirmed by XRD and IR absorption studies. The results reveal that for pH $< 3.8$, only jarosite is formed. As pH is increased a mixture of jarosite and SPM goethite precipitate. The relative amounts of the two phases however are different
for different concentrations. This could again be due to the variation in the pH value during the hydrolysis. Above pH 5.0, only SPM goethite is obtained. (The infra red absorption spectra show traces of sulphate ions which could be either occluded or surface adsorbed.) The results reveal a close similarity to the hydrolysis of Fe$^{3+}$ ions in a sulphate medium and in the presence of NH$_4^+$ (A discussion is presented later.)

When drops of NH$_4$OH are added to the solution, pH increases to alkaline values locally and formation of a green coloured complex at the interface is observed. This gets transformed to a brown coloured precipitate (hereafter referred to as the immediate precipitate) which has been immediately filtered out and studied. The product has been identified as SPM α-FeOOH. The filtrate, after the removal of the immediate precipitate, is subsequently hydrolysed and the hydrolysis product has been found to be jarosite again since the pH of the filtrate has been low. Instead, when the immediate precipitate is left in the solution ultrafine particles of α-FeOOH form the nuclei for further formation of α-FeOOH. After ageing in the solution they grow in size and the end product after 5 days is only α-FeOOH. The final pH of the solution is around 2.8. The Mössbauer spectra of the immediate precipitates formed from 10% solutions and the precipitates aged for 5 days are shown in Fig. 8.9(a-d). It can be seen that the immediate precipitate is completely
superparamagnetic while, after ageing the precipitate for 5 days, some particles grow and show a hyperfine six-line pattern. The precipitate has also been aged for 34 days but the ratio of the amount of SPM particles to that of the antiferromagnetic (AFM) particles did not change considerably. It is also of interest to note that the α-FeOOH formed from the slow hydrolysis of the solutions for 5 days are always superparamagnetic at RT. Similar spectra have been obtained for the precipitates from 20% solution.

Formation of GR(II) in a sulphate medium and its oxidation to α-FeOOH has already been discussed in chapter VII. It should be noted that the formation of green rust requires both ferrous and ferric ions to be present. It is produced by the precipitation from the solution due to addition of NH₄OH. When a drop of alkali is added to the freshly prepared solution, the local pH at the solution-alkali interface is very high; some of the ferrous ions get oxidised to ferric ions and green rust II is precipitated. A formula 2Fe(OH)₃· 4Fe(OH)₂· FeSO₄· XH₂O has been proposed for GR(II) (Detournay et al, 1975). When dispersed in the solution, it has been seen that the green rust II is transformed on oxidation to α-FeOOH alone and form the nuclei for further formation of α-FeOOH. Once the nuclei are formed it has been seen that the same phase grows preferentially even in the unfavourable condition of low pH. The solution becomes depleted in SO₄²⁻ during the
formation of GR(II). During the oxidation of GR(II) α-FeOOH, it regains its original sulphate ion concentration.

The temperature dependence of the relaxation spectra of α-FeOOH have been used to estimate the anisotropy energy. The average anisotropy energy of superparamagnetic particles is given by (2-16) and can be written as,

\[ KV = kT \ln(\tau/\tau_0) \] ... (8-1)

Anisotropy constant can be calculated if particle size is measured from electron micrographs.

For the immediate precipitate obtained from 10% solution a superparamagnetic doublet has been obtained in RT Mössbauer spectrum. So this temperature (RT 23°C) is well above the SPM blocking temperature. At 82°K, 50% of the particles are superparamagnetic. Substituting \( T = 82°K \), and \( \tau/\tau_0 = 25 \) in (8-1) we obtain,

\[ KV = 3.6 \times 10^{-14} \text{ ergs} \]

the anisotropy energy for α-FeOOH. Transmission electron micrographs (Fig. 8.10) show that the particles are rod-shaped and have an average length of about 600 Å and a diameter of about 60 Å. Assuming cylindrical rods, average volume of the particles is 170 \( \times 10^{-20} \) cm\(^3\). So anisotropy constant \( K \) turns out to be,

\[ K = 1.3 \times 10^4 \text{ ergs/cm}^2. \]
The Mössbauer spectra of the aged precipitate recorded at different temperatures are shown in Fig. 8.11. The spectrum is a doublet at 350°C (superparamagnetic blocking temperature) and the sample is completely SPm while the Neel temperature of normal α-FeOOH is about 393°C. A plot of percentage of SPm particles at each temperature is given in Fig. 8.12. 50% of the particles are SPm at a temperature T = 320°C. The average anisotropy energy of the particles turns out to be 14.4 x 10^{-14} ergs. Transmission electron micrograph of the sample Fig. 8.10c show that the particles are again rod-shaped. The lengths of the particles lie in the range 800 Å to about 1500 Å. Dendritic growth of smaller rod-like particles on the larger rods is an interesting phenomena that can be seen clearly in this picture. It can be understood that in this aged sample the bigger rods give rise to a hyperfine pattern in the RT Mössbauer spectrum and the smaller particles growing dendritically show superparamagnetism.

As temperature is increased above RT, more and more of α-FeOOH is formed in the solutions of investigated concentrations. Also α-FeOOH formed at higher temperatures are found to be larger sized particles and more crystalline. The Mössbauer spectra of the product formed in 20%, 10% and 1% solution at 50°C and 80°C are shown in Fig. 8.13. The product from 20% solution obtained at RT is pure jarosite; at 50°C it is a mixture of jarosite and goethite.
and at 80°C, the product is only goethite (large sized).
A similar trend is observed in the case of the hydrolysis
products of 10% solution. The α-FeOOH formed initially
at 50°C is superparamagnetic at RT. In course of time broad
distribution of hyperfine fields appear suggesting that some
particles have grown up. Only α-FeOOH is formed from 1% solution at all temperatures since the pH is high.

Hydrolysis in boiling solutions of the investigated
concentrations always yield α-FeOOH. A 10% solution
boiled for 15 minutes forms α-FeOOH which show a broad
distribution of hyperfine fields in the Mössbauer spectrum.
Mössbauer spectra of this sample have been recorded at
temperatures higher than RT and they are shown in Fig. 8.14.
Boiling for 3-4 hrs produces large sized and more crystalline
particles of α-FeOOH and a sharper hyperfine patterns are
obtained even at RT (Fig. 8.15).

**Hydrolysis of iron ions in the presence of NH₄⁺ and SO₄²⁻**

The results clearly reveal the following facts:
For a given concentration of the iron in the solution, there
seems to be a threshold pH below which only jarosite is
formed and above this pH goethite also starts forming.
There could be another threshold pH above which only
goethite is formed. The threshold values of pH seem to
depend on the concentration of iron ions in the solutions
as well as the temperature of hydrolysis. In air bubbled
solution at RT, FeOHSO₄ is also formed along with jarosite.

The precipitates formed by slow hydrolysis have always been found to be ferric compounds. By a rapid precipitation on addition of liquor ammonia, the intermediate phase of green rust—a ferric ferrous complex, which however, again oxidises to α-FeOOH in the solution is formed. A comparison of the results of normal hydrolysis processes with those of hydrolysis of Fe³⁺ ions suggest that the hydrolytic process when no alkali is added to ferrous ammonium sulphate solution is essentially that of the ferric ions. These are considered in detail here. It is evident that the hydrolysis is preceded by the oxidation of ferrous to ferric ions.

The ferric ion hydrolysis and the complexation by sulphate ions have been extensively studied. It has been very well known that SO₄²⁻ can effectively involve itself in the coordination shell of the ferric ions during hydrolysis and the stability constants of the iron (III)—sulphate complexes being high, a sulphate can be easily precipitated.

Jarosites have been obtained in the hydrolysis products by the hydrolysis of the ferric ions in the sulphate medium. Margulis et al (1976) report that the primary phase of hydrolytic precipitation of Fe(III) in the system Fe₂(SO₄)₃·nH₂O where M = K, Na, NH₄ are crystals of jarosite MFe₂(OH)₆(SO₄)₂ and an amorphous sulphate
2Fe₂O₃ · SO₃ · 2H₂O. In Fe₂(SO₄)₃ · H₂O solution itself hydronium jarosite (H₃O)Fe₃(OH)₆(SO₄)₂ is formed. It has been further explored that jarosite is formed if the pH of the solution is less than a threshold value pHₜₘ which is given by the expression,

\[ \text{pH}_\text{th} = a \ln C_{Fe} + b \quad \cdots (8-2) \]

where \( a \) is a constant independent of the temperature, and \( b \) reflects the dependence of \( \text{pH}_\text{th} \) on the temperature. Both the constants depend on \( M \). The empirical values of \( a \) and \( b \) have been determined for different \( M \) and at different temperatures. The results of the present study of the hydrolysis products from ammonium ferrous sulphate solution also indicate as said earlier that it can be closely represented by the mechanism of hydrolysis of Fe₂(SO₄)₃ · NH₄OH · H₂O system as for the formation of jarosite is concerned. (The studies of Margulies et al., 1976 do not indicate the formation of \( \alpha \)-FeOOH.) A threshold pH which depends on the concentration of iron ions and the temperature does exist. Infact, as temperature is increased, more of \( \alpha \)-FeOOH is formed and therefore as has been found by Margulies et al., the \( \text{pH}_\text{th} \) decreases as one goes to higher temperatures.

A number of other previous studies (see for example Umetsu et al., 1977) of the hydrolysis of ferric ions have shown that in the presence of the SO₄²⁻ ions and at high
acidity a jarosite is formed. The $\text{Fe}_2\text{O}_3$-$\text{SO}_3$-$\text{H}_2\text{O}$ system has been investigated by Posnjak and Merwin (1965) and on the basis of their data, Carlson and Simons (1961) show that the stable compounds in the $\text{Fe}_2\text{O}_3$-$\text{SO}_3$-$\text{H}_2\text{O}$ system up to about $110^\circ\text{C}$ are $(\text{H}_3\text{O})\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2$ at high acidity and $\text{Fe}_2\text{O}_3$·$\text{H}_2\text{O}$ at low acidity. Maryanitschik and Zapols'kii (1972) report the formation of a jarosite $\text{M}_2\text{O}$·$3\text{Fe}_2\text{O}_3$·$4\text{SO}_3$·$7\text{H}_2\text{O}$ at $125-200^\circ\text{C}$ by the addition of $\text{M}_2\text{SO}_4$ ($\text{M} = \text{K, Na, NH}_4$) to $\text{Fe}_2(\text{SO}_4)_3$ solution, by their thermogravimetry and X-ray diffractometric study of the hydrolysis products.

Ujihira et al (1978) identify $\text{NH}_4\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2$ as the product of hydrolysis of 0.1 M $\text{Fe}_2(\text{SO}_4)_3$ solution in the presence of urea at temperatures 363 K; $\text{NH}_4^+$ ions for the formation of this complex are supplied by the moderate hydrolysis of urea.

$$(\text{NH}_4)_2\text{CO} + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2$$

and $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH} \rightarrow \text{NH}_4^+ + \text{OH}^-$

Ohyabu and Ujihira (1981) again find that the sodium jarosite $\text{NaFe}_3(\text{OH})_6(\text{SO}_4)_2$ is formed at 353 K by the hydrolysis of 0.1 M ferric nitrate solution on addition of $\text{Na}_2\text{SO}_4$ solution at pH 1.5 and 1.8. At 363 K, a mixture of sodium jarosite and $\alpha$-$\text{FeOOH}$, and only $\alpha$-$\text{FeOOH}$ is obtained at 373 K. Results of the present study are also similar.

For example, the hydrolysis of 20% ammonium ferrous
sulphate solution where at RT only aminojarosite is obtained and as temperature is increased, a mixture of jarosite and goethite are obtained and above 80°C only goethite is obtained. Therefore the results of Ujihira et al. (1981) can also be explained in view of the discussion that has been made above as regards the threshold pH for the formation of jarosite. The threshold pH decreases as temperature is increased and therefore formation of goethite at higher temperature in solutions of the same iron ion concentration and pH can be understood.

FeOH\textsubscript{2}SO\textsubscript{4} has been found to precipitate from acidic Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} solutions at high H\textsubscript{2}SO\textsubscript{4} concentration (\sim 55 g/L) at temperatures of 185 - 200°C (Umetsu and Sasaki, 1976) by the reaction,

\[
\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} \rightarrow \text{FeOH}_2\text{SO}_4 + \text{H}_2\text{SO}_4
\]

Carlson and Simmons (1961) show that it forms at 200°C at high acidity.

8.2.2: Corrosion Products of Iron in Ammonium Ferrous Sulphate Solution

Corrosion products of iron in ammonium ferrous sulphate solution formed at RT, 50°C, and 80°C have been identified.

The Mössbauer spectra of the corrosion products
formed in 10% and 20% solution at RT are shown in Fig. 8.16. The RT corrosion in both 10% and 20% solutions always form α-FeOOH, superparamagnetic in the initial stages. In course of time they grow up in size and after about 5 days, all the particles are large sized and show hyperfine patterns corresponding to an internal field of about 349 kOe. The lines are broad suggesting a distribution of hyperfine fields arising from a range of particle sizes.

It is interesting that jarosite is not at all found in the corrosion products even in 20% solution. This can be expected because, within the incubation period of nucleation of jarosite, pH of the solution rises rapidly to pH 5.0 and α-FeOOH can be nucleated either directly from the solution or by the formation and subsequent oxidation of the intermediate phase of green rust, as has been found in the hydrolysis of ammonium ferrous sulphate solution. This then favours the further formation and growth of α-FeOOH phase alone again in accordance with the results obtained in the hydrolysis studies. So, α-FeOOH alone is formed in the RT corrosion. Also, α-FeOOH phase being quite stable at RT, it does not transform to any other phase.

Corrosion in 20% solution at 50°C also gave only α-FeOOH. Fig. 8.1 shows the RT Mössbauer spectrum of this sample. It has partly superparamagnetic and partly
antiferromagnetic particles. A distribution of hyperfine fields is seen (typical hyperfine field value of about 341 kOe). Rate of formation of green complex is higher at this temperature and they transform to $\alpha$-FeOOH rapidly.

Surprisingly enough, corrosion at 82°C forms magnetite (along with some $\alpha$-FeOOH). Though from the study of hydrolysis of ammonium ferrous sulphate solution it is learnt that more and more of $\alpha$-FeOOH is expected at higher and higher temperatures. The formation of magnetite can be understood in the following way. The increased dissolution rate of iron at the high temperature involved, leads to supersaturation of the solution with ferrous hydroxide which directly undergoes hydrothermal decomposition into magnetite, as discussed in chapter VII.

8.3. SUMMARY

The systematic study of the hydrolysis products of 20% and 10% ammonium ferrous sulphate solution under different conditions of pH showed that there exists a threshold pH for a given concentration of iron in the solution and temperature, below which only jarosite is formed. At about pH $\geq 4.5$, only $\alpha$-FeOOH is formed. In air bubbled solutions FeOH$\text{SO}_4$ is detected.

In the presence of dissolved oxygen, oxidation invariably occurs in ammonium ferrous sulphate solution.
and therefore both ferrous and ferric ions are present in the solution. When pH of the solution is raised to about 5.5 and above by the addition of alkali, green rust (a ferrous-ferric complex) is formed and transforms to α-FeOOH immediately. The electron micrographs show that these particles are rod-like; on ageing, dendritic growth of smaller particles on the larger ones is seen. Anisotropy energy and constants could be evaluated for these α-FeOOH particles. The results also suggest: that once sufficient nuclei of α-FeOOH are formed, further formation and growth of α-FeOOH is favoured even in the otherwise unfavourable conditions of pH.

At higher temperatures, more and more of α-FeOOH is formed in the solutions of investigated concentration since the threshold pH shifts to lower pH values as temperature is increased. At temperatures above 80°C only α-FeOOH is formed. Boiling solution after 3–4 h produce large sized and crystalline particles of α-FeOOH which exhibit sharp hyperfine Mössbauer spectra even at RT.

By a comparative study of the results with previous studies of ferric ion hydrolysis, it can be inferred that Fe^{2+} ions oxidize to Fe^{3+} ions during normal hydrolysis and the products are formed by the subsequent hydrolysis of the ferric ions in the presence of SO_4^{2−} and NH_4^{+} ions.
The results obtained in the hydrolysis studies and the mechanisms of the formation of the products have been applied to explain the mechanisms of formation of $\alpha$-FeOOH as the only product in the corrosion of iron in ammonium ferrous sulphate solution at RT and 50°C. In corrosion at 82°C however, the hydrothermal decomposition of Fe(OH)$_2$ seems to be dominant producing large amounts of magnetite.
Table 8-1
Mossbauer parameters of $\text{NH}_4\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2$ and $\alpha$-FeOOH found in the hydrolysis products from 20% and 10% ($\text{NH}_4\text{SO}_4\cdot\text{FeSO}_4\cdot6\text{H}_2\text{O}$) solution.

<table>
<thead>
<tr>
<th>Mother Liquor</th>
<th>Phase</th>
<th>Temp. $H$ (kOe)</th>
<th>Present work</th>
<th>Previous work</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\Delta$ (mm/s)</td>
<td>$\delta$ (mm/s)</td>
<td>$\Gamma$ (mm/s)</td>
</tr>
<tr>
<td>20% $\text{NH}_4\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2$</td>
<td>RT</td>
<td>-</td>
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<td>0.40</td>
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<tr>
<td></td>
<td>NH$_4$Fe$_3$(OH)$_6$(SO$_4$)$_2$</td>
<td>85$^0$K</td>
<td>-</td>
<td>1.22</td>
</tr>
<tr>
<td>10% $\text{NH}_4\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2$</td>
<td>RT</td>
<td>-</td>
<td>1.00</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>$\alpha$-FeOOH</td>
<td>RT</td>
<td>SPM</td>
<td>0.60</td>
</tr>
</tbody>
</table>

* Hryniewicz et al (1965)
$^I$ Takano et al (1968)
**Table 8-2**

XRD pattern of the aminojarosite

<table>
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<tr>
<th>2\theta (Mo-Kα)</th>
<th>d</th>
<th>I/I₀</th>
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<th>d</th>
<th>I/I₀</th>
<th>hkl</th>
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<td>6.90</td>
<td>5.89</td>
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<td>5.18</td>
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<td>012</td>
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<td>10.70</td>
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<td>5</td>
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I. Precipitate from 20% ammonium ferrous sulphate solution.
Table 8-3
Relative amounts of the aminojarosite and α-FeOOH formed from ammonium ferrous sulphate solutions with different initial pH

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<tr>
<th>Initial pH</th>
<th>20% solution</th>
<th>10% solution</th>
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<tr>
<td></td>
<td>amino-jarosite</td>
<td>α-FeOOH</td>
</tr>
<tr>
<td>3.8</td>
<td>100</td>
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<td>4.0</td>
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<td>22</td>
<td>78</td>
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<tr>
<td>6.0</td>
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</table>

*amounts in percent.
Fig 8.1. Room temperature Mössbauer spectrum of ammonium ferrous sulphate.
FIG. 8.2—MOSSBAUER SPECTRA OF THE HYDROLYSIS PRODUCT FROM 20% AMMONIUM FERROUS SULPHATE SOLUTION RECORDED AT (a) RT (b) 85°K
FIG. 8.3 - X-RAY DIFFRACTION PATTERN OF THE AMINOJAROSITE FORMED BY THE HYDROLYSIS OF 20% AMMONIUM FERROUS SULPHATE SOLUTION. 
(See table 8-13)
**Fig. 8.4** Room temperature Mössbauer spectra of products of hydrolysis of (a) 20%, (b) 10%, and (c) 1% ferrous ammonium sulphate solution.
FIG. 8.5 - INFRARED ABSORPTION SPECTRA OF THE HYDROLYSATES FROM (a) 20% AND (b) 1% SOLUTION. THE FORMER PRODUCT IS AMINO JAROSITE AND THE LATTER IS MOSTLY GEOTHITE.
Fig. 8.6 Mössbauer spectra of the precipitate from air bubbled 10% ferrous ammonium sulphate solution at (a) 298°K and (b) 82°K.
Fig. 8.7 Mössbauer spectra of the hydrolysates obtained from 20% solutions with different initial pH: (a) pH 3.8, (b) pH 4.0, (c) pH 4.5 and (d) pH 6.0. Ageing period: 5 days.
Fig. 8.8 Mössbauer spectra of the hydrolysates obtained from 10% solution with different initial pH
(a) pH 3.3, (b) pH 4.0, (c) pH 4.5, (d) pH 6.0.
Ageing period: 5 days.
Fig. 8.9 MOSBBAUER SPECTRA OF α-FE$_2$O$_3$ FORMED IN 10% FERROUS AMMONIUM SULPHATE SOLUTION AT pH 6.0: IMMEDIATE PRECIPITATE AT (a) RT, (b) 85°K, AND PRECIPITATE AGED FOR 5 DAYS AT (c) RT, (d) 110°K
Fig. 8.10  
(a) Scanning electron micrograph of jarosite formed from 20 \% solution.
(b) Transmission electron micrograph of the 'immediate-precipitate' (\alpha-\text{FeOOH}) from 10 \% solution at pH 6.0.
(c) Transmission electron micrographs of the aged-precipitate (ageing period: 5 days) from 10 \% solution (pH 6.0).
Fig. 8.11 Mössbauer spectra of aged precipitate (from 10% solution at pH 6.2) recorded at different temperatures.
Fig. 8.12. Percentage of superparamagnetic $\alpha$-FeOOH in the aged precipitate (from 10% solution at pH 6.2), at different temperatures.
FIG. 8.13: MöSSBAUER SPECTRA OF THE HYDROLYSIS PRODUCTS OF 20% SOLUTION FORMED AT (a) 50°C, AND (b) 80°C FROM 10% SOLUTION FORMED AT (c) 50°C AND (d) 80°C FROM 1% SOLUTION FORMED AT (e) 50°C AND (f) 80°C.
FIG. 8.14 MOSSBAUER SPECTRA OF $\alpha$-FeOOH FORMED FROM BOILING AMMONIUM FERROUS SOLUTION IN 15 minutes RECORDED AT DIFFERENT TEMPERATURES.
FIG. 8.15 - Mössbauer spectrum of α-FeOOH formed in boiling ammonium feroous sulphate solution in 4 hours.
Fig. 8.16 Mössbauer spectra of RT corrosion products of electrolytic iron in a) 10% solution for 1 day, b) 10% solution for 10 days and c) 20% solution for 5 days.
FIG. 8.17 - MöSSBAUER SPECTRUM OF THE CORROSION PRODUCT IN 20% AMMONIUM FERROUS SULPHATE SOLUTION AT 50°C IS SHOWN (Corrosion period 2 days)
CHAPTER IX

CONCLUSIONS

The corrosion of iron in aqueous solutions resulting in the formation of various oxides and oxyhydroxides has been studied for many years. But detailed investigations of the processes and products, and especially a study of the formation of intermediate green complexes or rusts and their subsequent transformation, are of more recent origin. (Bernal et al., 1959; Misaka et al., 1974; McGill et al., 1976). The results of investigations of the corrosion products have been interpreted to form a reaction sequence (Kasimir et al., 1982) such studies have adequately described the overall reactions. From the present investigations the sequences of appearance of the various insoluble products (of the corrosion reaction of iron in aqueous ammonium salt solutions) have been followed. The trends in the reaction sequences are in general agreement with the results obtained by a number of previous investigators under closely related conditions.

By an extensive study of the corrosion products of electrolytic iron in 45% ammonium nitrate solution, the conditions for the formation of various products could be particularised. If it is found for example, that the hydrolysis of iron in NH₄NO₃ solution produces α-FeOOH at pH < 3.0 and γ-FeOOH at pH 3.0 < pH < 5.0 both α-FeOOH and ferrhydrite are formed. Even at pH > 5.6, small
quantities of $\alpha$-FeOOH are formed by the dissolution–precipitation mechanism from $\gamma$-FeOOH. Green rust and magnetite are formed at the metal–solution interface during corrosion in the absence of free access to oxygen. At temperatures higher than RT, a film of magnetite is formed on the metal and $\alpha$-Fe$_2$O$_3$ is precipitated from the bulk of the solution. The formation of hydrous $\alpha$-FeOOH during corrosion of electrolytic iron in 45% NH$_4$NO$_3$ solution of initial pH 1.0 is another important result obtained in the present study.

Of the three types of iron powders studied here, corrosion rate is found to be highest for cast iron and least for electrolytic iron. The major products of corrosion are also different for each type of iron. Magnetite is found to be the major product of corrosion of reduced iron under most of the conditions while, in the RT corrosion of cast iron, $\gamma$-FeOOH is formed initially and part of it subsequently transforms to magnetite by a dissolution–precipitation mechanism. The products of corrosion of cast iron at higher temperatures are found to sensitively depend on the ratio of the reactants. Further investigations taking into account the effects of the impurities and the surface textures of these iron powders, are however desirable.

Corrosion of iron in ammonium sulphate and ammonium ferrous sulphate showed that $\alpha$-FeOOH is the major product formed in the presence of SO$_4^{2-}$ ions. In (NH$_4$)$_2$SO$_4$ solution
for example, even though $\gamma$-FeOOH is the initial product, a large part of it undergoes transformation to $\alpha$-FeOOH by a dissolution-precipitation mechanism. At temperatures slightly above RT, the formation of $\alpha$-FeOOH via the intermediate phase of green rust is favoured.

$\beta$-FeCOOH which is generally expected to form in the presence of $\text{Ca}^{2+}$ ions has not been found in the corrosion products (of iron in ammonium chloride solution) in agreement with the results of Ohyabu and Ujihira (1980) and Hamada and Kuma (1976). Large amounts of magnetite are however formed via the intermediate phase of Green complex I (GCI).

The hydrolysis studies of ammonium ferrous sulphate solution showed that sulphate-complexation is strong at low pH values and that, below a threshold pH (which depends on the concentration of iron in the solution and the temperature), only jarosite is formed and, above the threshold pH, $\alpha$-FeOOH is also formed. The present work also identifies Fe(OH)SO$_4$ as one of the products of hydrolysis.

The hydrolysis products precipitated from Fe$^{3+}$ salt solutions and the amion effect is the pH range 1-2 has been studied by Ohyabu and Ujihira (private communication).

Table 9-1 shows the relationship between the iron(III) compounds precipitated from the iron salt solutions and their stability constants. It can be seen that $\alpha$-FeOOH is the precipitate formed in the presence of NO$_3^-$ (\(\alpha\)-FeOOH
is obtained as the product at pH 3.0 in NH₄NO₃ solution) and a jarosite in the presence of sulphate (hydrolysis of ammonium ferrous sulphate at pH < 3.8 produces amino-jarosite). The anion content in the precipitate shows that larger the stability constant more are the anions included into the hydrolysis products precipitated.

The phase transformation in the corrosion process is found to be well understood in terms of their relative Gibb's free energies of formation ΔG⁰ (Meisel, 1981). The ΔG⁰ level diagram is shown in Fig. 9.1. Mössbauer spectroscopic phase analysis has always showed that the rust consists of more than one phase, the relative concentrations of which depend on the corrosion character of the atmosphere. Higher the corrosivity, higher is the concentration of those phases which are found in the lower part of the Fig. 9.1. Thus for example, α-Fe₂O₃, the most stable of all the iron oxides is formed under extreme conditions of corrosion, and at high temperatures. γ-FeOOH has been found to be the initial product formed during corrosion in aqueous solutions but under aggressive conditions, it transforms to its more stable polymorph α-FeOOH. Thus the formation of α-FeOOH by the dissolution-precipitation mechanism from γ-FeOOH encountered at many places in the present thesis can be understood. The present study also suggests that the formation of α-FeOOH is favoured in the presence of $S\,^{2-}_4$ ions.
The physical changes like pitting, etching, formation of iron oxide phases occurring on the surface of the sheet has been followed in the present study by scanning electron microscopy and the composition of the corrosion film has been deduced by X-ray diffractometry. But the initial stages of the corrosion process in the physico-chemical sense has to be followed using electron spectroscopy for chemical analysis (ESCA). This would enable a study of the monolayers of the product on the surface of the sheet. Further advanced stages of oxidation of the surface can be followed by the resonance detection of conversion electrons, X-rays, and γ-rays.

In the present study, only the insoluble products of corrosion precipitated from the bulk of the solution at the metal-solution interface have been studied. But it is highly desirable to obtain information about the hydrolytic processes of the iron aquo-ion in solution before precipitation. Frozen-solution studies following the dissolution of iron at different pH values would be invaluable in giving a clearer picture of the hydrolytic processes leading to the precipitation of the solid products. These are essential to form a complete model of the corrosion process in aqueous solutions.
Table 9-1

Relationship between iron(III) compounds precipitated and stability constants

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<th>ClO$_4^-$</th>
<th>NO$_3^-$</th>
<th>Br$^-$</th>
<th>Cl$^-$</th>
<th>SO$_4^{2-}$</th>
<th>F$^-$</th>
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<tr>
<td>Stability constant</td>
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<td>0.36</td>
<td>1.03</td>
<td>2.21</td>
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<td>5</td>
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</tr>
<tr>
<td>Precipitate</td>
<td>α-FeOOH</td>
<td>α-FeOOH</td>
<td>β-FeOOH</td>
<td>NaFe$_3$(SO$_4$)$_2$(OH)$_6$</td>
<td>γ-FeOOH</td>
<td></td>
</tr>
<tr>
<td>Anion content (atomic ratio)</td>
<td>Br/Fe = 0.012</td>
<td>Cl/Fe = 0.15</td>
<td>SO$_4$/Fe = 0.67</td>
<td>F/Fe = 0.55</td>
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<td>Compound</td>
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Fig. 9.1 Free enthalpies of formation $\Delta G^\circ$ of some corrosion products of iron relative to $\alpha$-Fe$_2$O$_3$