CHAPTER VII

CORROSION OF IRON IN AMMONIUM SULPHATE AND AMMONIUM CHLORIDE SOLUTIONS

Corrosion products of iron in ammonium sulphate and ammonium chloride solutions have not been studied in detail previously. Ujihira et al (1978) have identified a ferric compound from the conversion electron Mössbauer spectra of the corrosion products on the surface of NT-70H steel, dipped in 0.25 M (NH₄)₂SO₄ and 0.5 M NH₄Cl solution.

The products of corrosion of electrolytic iron in 10% ammonium sulphate and 10% ammonium chloride solutions have been studied here. The results of these studies are presented and discussed in this chapter.

7.1. PREPARATION OF SAMPLES

Corrosion of 4 gms of electrolytic iron powder in 100 ml each of 10% (NH₄)₂SO₄ solution (initial pH 5.2) and 10% NH₄Cl solution (initial pH 4.6) has been carried out at RT, 54°C and 82°C for different lengths of time. pH has been monitored during corrosion and in some cases, the separation of the products into R₁ and R₂ has been done as described in section 5.1. Corrosion of iron sheets (1 m²) in 50 ml of each solution (as-prepared) has also been carried out at RT.
In \((\text{NH}_4)_2\text{SO}_4\) solution corrosion has been carried out at constant pH 2.5 and 3.5 for 3 hours and the products have been studied. A constant pH is maintained by the addition of drops of 5N \(\text{H}_2\text{SO}_4\). Green rust is precipitated from the filtrates by the addition of ammonia, subsequent transformations of green rust under a few conditions have been followed.

7.2. RESULTS AND DISCUSSIONS

7.2.1. Corrosion in \(10\% \ (\text{NH}_4)_2\text{SO}_4\) Solution

Room temperature corrosion

Variation of pH of the solution during the corrosion reaction of 4 gms of electrolytic iron in 100 ml of the \(10\%\) solution is shown in Fig. 7.1. pH of the solution initially increases very fast. After attaining a pH of about 7, it fluctuates due to the effect of combined processes of dissolution and hydrolysis which tend to change the pH in opposite directions, as has been discussed in section 5.3.

It has been well established that the dissolution of iron is strongly accelerated by the presence of sulphate ions. Apart from the complexing ability of \(\text{NH}_4^+\) ions, the complexing of iron by sulphate ions have also been extensively studied. In deaerated solution, the corrosion is smaller than in the \(\text{NH}_4\text{NO}_3\) solution; since in the latter, \(\text{NO}_3^-\) ions
are the oxidising agents in the absence of air. Aer ation greatly enhances the corrosion rate in 10% (NH$_4$)$_2$SO$_4$ solution (it is even higher than the corrosion rate of electrolytic iron in 45% NH$_4$NO$_3$ solution). The dissolution rate of iron therefore seems to be controlled by both hydrogen evolution and oxygen depolarisation reactions. The overall reaction is therefore,

$$\text{Fe} + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O}. \quad \ldots (7-1)$$

Also, the ratio of the rate of corrosion of iron in (NH$_4$)$_2$SO$_4$ solution in the absence of air to that in the presence of air is about 0.17 (Mellor, 1934). The chemical-electrochemical mechanism of corrosion of iron in neutral (NH$_4$)$_2$SO$_4$ solution has been studied in detail by Kuznetsora and Zhuk (1977). The mechanisms are said to be governed by diffusion kinetics.

**Products of RT corrosion**

The Mössbauer spectra of the products of RT corrosion for different lengths of time are shown in Fig. 7.2. The results of the analyses of these spectra are summarised in Table 7-1. Fig. 7.3 shows the relative amount of each phase formed in the RT corrosion as a function of time.

Room temperature corrosion initially forms mainly γ-FeOOH. Traces of magnetite are also seen. As corrosion
progresses, more and more of $\alpha$-FeOOH and magnetite are formed. In a 10-day corrosion sample, $\gamma$-FeOOH is lesser while, almost equal amounts of $\alpha$-FeOOH and magnetite are found. Also $\alpha$-FeOOH is not superparamagnetic and shows hyperfine splitting. A plot of the intensities of the most intense X-ray line of each phase in these diffractograms are shown in Fig. 7.4. The amount of $\gamma$-FeOOH is seen to decrease, while that of $\alpha$-FeOOH and magnetite increase. The diffractograms have been shown only to demonstrate qualitatively that $\gamma$-FeOOH is getting transformed to other products. Since only line intensities (of the most intense lines) are plotted no quantitative conclusions can be made. The corrosion of iron sheet in the solution for about 15 days showed $\gamma$-FeOOH as the only product. When a 1 mil thick electrolytic iron foil is corroded in the solution, the foil is completely corroded away in about 25 days and the product is again seen to be only $\gamma$-FeOOH.

These results suggest that during the corrosion of iron powder, corrosion rate is high and large amounts of $\gamma$-FeOOH are formed initially by the hydrolytic precipitation, and then undergo dissolution, reprecipitation to $\alpha$-FeOOH and magnetite. $\gamma$-FeOOH being less stable, it readily transforms to its polymorph $\alpha$-FeOOH when the conditions are favourable. Presence of strongly coordinating sulphate ions seems to favour (Ujihira and Ohyabu, 1979) the formation of $\alpha$-FeOOH. $\gamma$-FeOOH therefore undergoes dissolution and $\alpha$-FeOOH is
precipitated as discussed in section 5.3. Magnetite can also be formed by the reductive dissolution of $\gamma$-FeOOH as has been discussed in section 6.2.2. Though in sulphate medium, the formation of green rust is favoured, under the prevailing conditions, the formation of green rust and its subsequent oxidation does not seem to be an important mechanism of the formation of products in RT corrosion.

The mechanisms of formation and (the sequences of the reaction) of the products can be schematically represented as,

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe(OH)}^+ \rightarrow \text{Fe(OH)}_2^+ \\
\text{Fe} & \rightarrow \text{Fe(OH)}^+ \rightarrow \text{Fe}_3\text{O}_4 \\
\text{Fe}_3\text{O}_4 & \rightarrow \gamma\text{-FeOOH} \rightarrow \alpha\text{-FeOOH}
\end{align*}
\]

where $O$ stands for oxidation, $O_r$ for rapid aerial oxidation and $O_s$ for slow oxidation.

Corrosion at constant pH 2.5 formed a brown precipitate which is identified as FeOOH. The filtrate is brownish orange in colour. When the pH of the filtrate is raised to alkaline values by the addition of liquid ammonia, green rust is precipitated. The green rust oxidises very fast and during filtration and drying it got partly oxidised. Fig. 7.5a shows the Mössbauer spectrum of a partially oxidised green rust sample. The
spectrum is somewhat similar to that obtained by Pritchard and Mould, (1971) for partially oxidised Fe(OH)$_2$. The spectrum can be resolved into contributions from a doublet of SPM $\alpha$-FeOOH and $\gamma$-FeOOH and that of green rust. The Mössbauer pattern of green rust comprises of doublet due to Fe$^{2+}$ ions and a singlet of, Fe$^{3+}$ ions (Gancedo et al., 1976). The Mössbauer parameters of the green rusts are given in table 7-2. The green rust expected in the presence of sulphate medium is of the second variety.

Fig. 7.5c shows the Mössbauer spectrum of the completely oxidised green rust. It is mostly a doublet due to SPM $\alpha$-FeOOH (a hazy hyperfine pattern of $\alpha$-FeOOH is also seen) and small quantities of $\gamma$-FeOOH. X-ray diffractograms show lines due to $\alpha$-FeOOH, $\gamma$-FeOOH and small amounts of $\left(NH_4\right)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$. The formation of ferrous ammonium sulphate is an interesting observation made here. It is possible that some NH$_4^+$ ions are also bound to the green rust which is formed and have not been removed during washing. Subsequently, in the wet condition, the Mohr's salt must have been precipitated. Alternatively, it might have formed during precipitation of green rust by the addition of alkali.

When the solution in which green rust is formed is diluted with a large amount of distilled water, the green rust is found to transform immediately to a black
precipitate. This product is identified as Fe$^{2+}$-rich magnetite by its Mössbauer spectrum Fig. 7.6a. By the addition of a large amount of water, pH immediately falls below pH 7.0. Green rust is unstable in a slightly acid solution and undergoes a solid state transformation to Fe$_3$O$_4$ (Smith and McEnaney, 1979). The spectrum is strikingly similar to that of the product obtained by hydrothermal decomposition of ferrous hydroxide (Pritchard et al., 1971). Small amounts of γ-FeOOH are also seen. If this black precipitate is left in the mother liquor for a few days, it oxidises to α-FeOOH and γ-FeOOH. The Mössbauer spectrum of this sample is shown in Fig. 7.6.

**Corrosion at temperatures higher than RT**

Fig. 7.7 shows the Mössbauer spectra of the corrosion products obtained at 54°C and 82°C for different lengths of time. At 54°C, in one hour corrosion, considerable amount of (SPM) α-FeOOH is already formed along with some γ-FeOOH, as is clearly seen from the infra-red spectrum of the sample. The Mössbauer spectrum, Fig. 7.7, however shows only a doublet which corresponds to γ-FeOOH and SPM α-FeOOH. The major product of corrosion after 2 days however is larger sized α-FeOOH showing hyperfine pattern in the Mössbauer spectrum Fig. 7.7; traces of γ-FeOOH and magnetite are also found. γ-FeOOH formed initially may subsequently undergo dissolution-precipitation
to $\alpha$-FeOOH. Also, in the sulphate medium, the ferrous species in the solution can transform to the intermediate compounds viz., green complex (GC) II or green rust (GR) II (Misawa et al., 1974) which finally gets oxidised to $\alpha$-FeOOH. This reaction is seen to be accelerated as the temperature is increased above RT (the solution looks green in colour suggesting that a GC is formed).

The sequence of reaction is,

$$Fe(OH)_2 \rightarrow GC\ II\ or\ GR\ II \rightarrow \alpha$-FeOOH.$$ \hspace{1cm} ... (7-3)

During the first stage of the reaction, the solution becomes depleted in $Fe^{2+}$, $Fe^+$ and $SO_4^{2-}$ ions. It regains its initial $SO_4^{2-}$ concentration in the second stage. The formation of large amounts of $\alpha$-FeOOH at $54^\circ{C}$ can thus be understood.

Magnetite can be formed either by the reductive dissolution of $\gamma$-FeOOH or by the slow oxidation of Fe(OH)$_2$ or GC II and GR II. The possible mechanisms of formation of the various products found in corrosion at $54^\circ{C}$ can be schematically written down as follows:

$$Fe \rightarrow Fe(OH)^+ \rightarrow Fe(OH)_2 \rightarrow \gamma$-FeOOH \hspace{1cm} DP$$

$$Fe(OH)_2 \rightarrow GC\ II \rightarrow \alpha$-FeOOH \hspace{1cm} R$$

$$Fe_3O_4 \leftarrow R$$

...(7-4)
Slow Oxidation, \( O_s \); Rapid aerial oxidation, \( O_r \); oxidation, DP= Dissolution-precipitation; R = Reductive dissolution-precipitation.

Fig. 7.8 shows the Mössbauer spectra of the products formed at 82°C for 8 h and for 2 days. It is interesting to find that both the initial and final major product of corrosion is magnetite. It is evident that the magnetite here is not formed by the transformation of \( \gamma \)-FeOOH as in RT corrosion, nor by the intermediate phase of green rust. It could possibly be formed by the hydrothermal decomposition of ferrous hydroxide supersaturating the solution. The reaction can take place as follows:

\[
3\text{Fe(OH)}_2 \xrightarrow{82^\circ C} \text{Fe}_3\text{O}_4 + 3\text{H}_2\text{O} \quad ...(7-5)
\]

The magnetite formed here is also almost stoichiometric as can be seen from Fig. 7.8, while the magnetite formed by a surface reaction always seems to be nonstoichiometric since the stoichiometry depends on the ionic transport at the surface. Even the magnetite formed by the transformation of green rust will be in most cases nonstoichiometric since the transformation is only topotactic.
7.2.2. Corrosion in 10 % NH₄Cl Solution

Corrosion at RT

Variation on pH of the solution during the corrosion reaction of 4 gms of electrolytic iron powder in 100 ml of the solution is shown in Fig. 7.9. The pH increases initially upto about 6.8 and then decreases levelling off around pH 6.2. It is known that corrosion rate in NH₄Cl solution is very small in deaerated solutions. However, it has been observed in the present study that the rate of corrosion in aerated 10 % NH₄Cl solution is larger than in the aerated 45 % NH₄NO₃ solution. As in the case of corrosion in (NH₄)₂SO₄ solution, the corrosion here also, seems to be controlled by both hydrogen evolution and by oxygen depolarisation reaction. Further, like the SO₄²⁻ ion, the Cl⁻ ion is a complexing ion and hence in the presence of oxygen, the corrosion rate is expected to be higher than in the nitrate solution. Fig. 7.10 shows the Mössbauer spectra of the products of RT corrosion for different lengths of time. The initial product of corrosion is found to be γ-FeOOH. Some amount of γ-FeOOH formed initially deposits on the walls and bottom of the corrosion cell. X-ray diffraction pattern of the one-day sample show the presence of small quantities of superparamagnetic magnetite also. As corrosion progresses, larger amounts of magnetite are formed. The Mössbauer spectrum of the 7-day sample (R₄)
for example Fig. 7.10c has a large amount of magnetite (Fe$_{2.85}$O$_4$) while the residue R$_2$ (along with the deposits on the wall) has mostly γ-FeOOH. These are confirmed by X-ray diffraction and IR studies. The results therefore suggest that magnetite is formed by the transformation of γ-FeOOH precipitated from the solution. It could have formed by a continuous reductive dissolution of γ-FeOOH. Only traces of α-FeOOH are found in the products of 7-day corrosion. β-FeOOH which is believed to be produced by the corrosion of iron in chloride solutions has not been detected. It should be noted that Hamada and Kuma (1976) and Jujihira and Nomura (1980) also do not find β-FeOOH during corrosion of iron (steel) in NaCl solution.

Corrosion of iron sheet in 10% NH$_4$Cl solution shown that γ-FeOOH is almost the only product of corrosion. Even after 15 days of corrosion, no detectable amount of magnetite is formed. No crust of γ-FeOOH is formed on the surface of the solution. A foil of 1 mil thickness immersed in the solution had completely dissolved in about 20 days and γ-FeOOH is the only product found. In the corrosion of powder, huge amounts of γ-FeOOH are formed; the reductive dissolution of γ-FeOOH leads to the precipitation of magnetite.

Corrosion at temperatures above RT

Fig. 7.11 shows the Mössbauer spectra of the products formed at 54°C. The product (in one-hour corrosion)
is identified to be only γ-FeOOH from all studies. The Mössbauer spectrum of a 2-day corrosion product (Fig. 7.11c) shows patterns from magnetite, γ-FeOOH. A green complex is seen to be formed during corrosion (the solution becomes green coloured). It is known (Detournay et al., 1975) that in chloride solutions Green rust I is formed. It is also known to transform to γ-FeOOH by rapid aerial oxidation and to magnetite by slow oxidation (Misawa et al., 1974). Magnetite may therefore be formed both by the oxidation of green rust and by reductive dissolution of γ-FeOOH, itself being formed by either the rapid oxidation of GR or by precipitation from Fe(OH)_2 ions produced on rapid aerial oxidation of FeOH^+ ions. Small amounts of α-FeOOH might be formed by the dissolution reprecipitation from γ-FeOOH. Schematic of mechanism of formation of products at RT and at 54°C is indicated below,

\[
\begin{align*}
\text{Fe(OH)}_2^+ & \xrightarrow{\text{DP}} \alpha\text{-FeOOH} \\
\text{Fe} & \xrightarrow{0} \text{Fe(OH)}^+ \\
\text{Fe(OH)}_2^+ & \xrightarrow{0} \gamma\text{-FeOOH} \\
\end{align*}
\]

(7-6)

At 82°C, again, the product is seen to be mostly magnetite, as in the case of corrosion in (NH_4)_2SO_4 solution. It could be forming by the hydrothermal decomposition of ferrrous hydroxide as discussed earlier.
7.3. SUMMARY

The mechanisms of formation of the product during corrosion of iron in NH₄Cl solution are very much similar to that in (NH₄)₂SO₄ solution except for the following differences that arise due to the anion effect. The intermediate phase of green rust or complex is expected to be of the first type in chloride solution and of the second type in sulphate solution. Green rust I is known to transform to γ-FeOOH on rapid oxidation and to magnetite by slow oxidation while GR II or GC II is known to transform to α-FeOOH mainly. Also, the presence of SO₄²⁻ ions seem to favour the formation of α-FeOOH and in the chloride solution therefore the dissolution-precipitation from γ-FeOOH leads to mainly magnetite and only traces of α-FeOOH are found to be formed. At RT, γ-FeOOH is formed by rapid aerial oxidation of the ferrous species. When formed in large amounts, γ-FeOOH simultaneously undergoes dissolution and, α-FeOOH and Fe₃₋ₓO₄ are reprecipitated from the solution. At 54°C, large amounts of α-FeOOH are formed via the intermediate phases of Green complex II. At 82°C, the hydrothermal decomposition of ferrous hydroxide seems to be dominant producing stoichiometric magnetite. Precipitation of green rust by the filtrate using alkali and its subsequent solid state transformation to magnetite by a rapid solid state transformation and to other products by aerial oxidation have been studied at RT.
The mechanisms of formation of the products during corrosion of iron in NH₄Cl solution are very much similar to that in (NH₄)₂SO₄ solution except for the following differences that arise due to the anion effect. The intermediate phase of green rust or complex is expected to be the first type in chloride solution and of the second type in sulphate solution. Green rust I is known to transform to γ-FeOOH on rapid aerial oxidation and to magnetite by slow oxidation, while GR II or GC II is known to transform to α-FeOOH mainly. Also, the presence of SO₄²⁻ ions seem to favour the formation of α-FeOOH, but in the chloride solution the dissolution–precipitation from γ-FeOOH leads mainly to magnetite, and only traces of α-FeOOH. At 82°C, magnetite is expected to be formed by the decomposition of Fe(OH)₂ as in the case of corrosion in ammonium sulphate solution.

It is surprising that β-FeOOH which is the usual product of hydrolysis of ferric ions in the presence of Cl⁻ ions, is not found here, in agreement with the results of Ujihira and Nomura (1980) and Hamada and Kuma (1976).
### Table 7-1

Corrosion products of electrolytic iron in $(\text{NH}_4)_2\text{SO}_4$ and NH$_4$Cl solution at different temperatures

<table>
<thead>
<tr>
<th>Corrosion Medium</th>
<th>RT</th>
<th>54°C</th>
<th>82°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{NH}_4)_2\text{SO}_4$</td>
<td>$\gamma$-FeOOH (initial product)</td>
<td>$\gamma$-FeOOH (initial product)</td>
<td>Fe$_{3-x}O_4$</td>
</tr>
<tr>
<td></td>
<td>$\alpha$-FeOOH</td>
<td>$\alpha$-FeOOH</td>
<td>$\gamma$-FeOOH$^*$</td>
</tr>
<tr>
<td></td>
<td>Fe$_{3-x}O_4$</td>
<td>Fe$_{3-x}O_4$</td>
<td>$\alpha$-FeOOH$^*$</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>$\gamma$-FeOOH</td>
<td>$\gamma$-FeOOH</td>
<td>Fe$_{3-x}O_4$</td>
</tr>
<tr>
<td></td>
<td>Fe$_{3-x}O_4$</td>
<td>Fe$_{3-x}O_4$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\alpha$-FeOOH$^*$</td>
<td>$\alpha$-FeOOH</td>
<td></td>
</tr>
</tbody>
</table>

* very small quantities.
<table>
<thead>
<tr>
<th>Green rust</th>
<th>Gancedo et al (1974)</th>
<th>Present work</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta$ (mm/s)</td>
<td>$\Delta$ (mm/s)</td>
</tr>
<tr>
<td>I</td>
<td>Fe$^{2+}$</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+}$</td>
<td>0.49</td>
</tr>
<tr>
<td>II</td>
<td>Fe$^{2+}$</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+}$</td>
<td>0.49</td>
</tr>
</tbody>
</table>
Fig: 7.1. Variation of pH of the solution during the corrosion reaction of 4 gms of electrolytic iron in 100 ml of 10% (NH₄)₂SO₄ solution.
FIG. 7.2 - MOSSBAUER SPECTRA OF THE PRODUCTS OF RT CORROSION IN 10% (NH₄)₂SO₄ SOLUTION FOR (a) 1 DAY, (b) 5 DAYS AND (c) 10 DAYS
The percentage area under Mossbauer resonance of the various products (shown in Fig. 7.2) formed during corrosion of iron in 10% (NH₄)₂SO₄ solution.
FIG. 7.4 THE VARIATION OF THE X-RAY DIFFRACTION LINE INTENSITIES OF THE PRODUCTS OF RT CORROSION IN (NH₄)₂SO₄ SOLUTION.
Fig. 7.5 (a) Mössbauer spectrum of partially oxidised green rust.
(b) Sample in (a) after 24 h.
(c) Sample in (a) after 10 days.
FIG 7.5- Mössbauer spectra of (a) the black precipitate (Fe$^{2+}$ rich magnitude) obtained by rapid solid state transformation of green rust by diluting the solution with large amount of water and (b) sample in (a) aged in the solution for about 5 days.
FIG. 7.7- MOSSBAUER SPECTRA OF THE PRODUCTS OF CORROSION IN (NH₄)₂ SO₄ SOLUTION AT 54°C FOR (a) 1 HOUR (Sample R₁) AND (b) 2 DAYS (R₁+ R₂)
FIG. 7.8—MÖSSBAUER SPECTRA OF THE PRODUCTS OF CORROSION IN (NH₄)₂ SO₄ SOLUTION AT 82°C FOR (a) 8 HOURS AND (b) 2 DAYS
Fig: 7.9. VARIATION OF pH OF THE SOLUTION DURING CORROSION OF 4gms OF ELECTROLYTIC IRON IN 100 ml OF 10% NH₄Cl SOLUTION.
Fig. 7.10 - Mössbauer spectra of RT corrosion products in NH₄Cl solution (a) 1 day (Sample R₁), (b) 1 day (Sample R₂), (c) 7 days (Sample R₁) and (d) 7 days (Sample R₂ + deposits on the walls of the corrosion cell)
Fig. 7.11 - Mössbauer spectra of the products of corrosion in NH₄Cl solution at 54°C for (a) 1 hour (Sample R₁) (b) 1 hour (Sample R₂) and (c) 2 days (R₁ + R₂)