Manganese (IV) oxide converts to water soluble manganese (II) sulphate after reduction with suitable reducing agent. Thermal reduction of MnO$_2$ with pyrite was investigated in the previous chapter. It is learnt from literature survey that reduction of MnO$_2$ is also being carried out in aqueous medium using reducing agents like sulphurous acid and ferrous sulphate. Pyrite, on aqueous oxidation gives ferrous sulphate. So it can be possible to get water soluble manganese sulphate in the suspended particle leaching of manganese dioxide along with pyrite. Further, there is a substantial difference in the rest potentials of manganese dioxide and pyrite in an electrolyte. So there is a possibility of galvanic interaction between the two. In the present chapter, the chemical as well as the galvanic interaction between manganese dioxide and pyrite in a mild sulfuric acid medium has been studied with a view to get into the details of reaction kinetics and mechanism. The work of this chapter comprises four types of studies;
these are, (i) suspended particle leaching of manganese dioxide, in which the effect of different reaction parameters like temperature, acid concentration, pyrite concentration, etc., on the leaching of manganese has been examined, (ii) measurements of electrochemical parameters like the rest and mixed potential and galvanic current with the help of which Evan's diagrams are obtained and studied, (iii) pellet leaching study in which the leaching values of manganese and iron are obtained and compared with the galvanic measurements, and (iv) examining the galvanostatic polarization curves.

4.1 EXPERIMENTAL:

Reagent, Solution and Glasswares:

The chemicals used in the experiments were all of reagent grade and double distilled water was used for preparing all the solutions. Whatever glasswares were of Pyrex or Corning variety.

4.1.1 SUSPENDED PARTICLE LEACHING OF MANGANESE DIOXIDE WITH PYRITE:

4.1.1.1 Apparatus:

The dissolution experiments were conducted in a two liter corning reaction vessel having a flanged cover with five openings made of standard joints. Stirring of the solution was done with a glass impeller
attached to a 1/12 h.p. motor whose rpm was regulated through a variable resistance and is checked time to time with a tacometer. The impeller was introduced into the reaction vessel through the central hole of the flanged cover and sealing arrangement was provided in order to prevent the escape of vapours during the experiment. The other openings were used for inserting a gas (oxygen) inlet tube, fixing a condenser and sample withdrawal. The entire assembly was inserted into a thermostatic bath that maintained the temperature. A schematic diagram of the experimental set up is shown in Fig. 4.1.

4.1.1.2 Materials :

The low grade manganese ore, synthetic $\beta$-MnO$_2$, shalypyrite and crystalline pyrite samples have been used in this chapter. Preparation and characterisation of all these samples have been presented in Chapter-II.

4.1.1.3 Experimental Procedure :

1500 ml. of distilled water with required concentration of sulphuric acid was taken in the reaction vessel and was allowed to attain the desired temperature by adjusting the control. The powdered sample mixtures were then charged into the reaction vessel through a funnel. The solution was kept stirred
Fig. 4.1 Schematic diagram of the experimental setup used for suspended particle leaching of manganese dioxide with pyrite.

1. Thermostatic Bath
2. Corning reaction vessel
3. Glass impeller
4. Oxygen inlet
5. Flange cover with four openings
6. Sealing device
7. Condenser
8. $\frac{1}{2}$ H.P. Motor
9. Mercury seal
throughout the experiment except for very small intervals for withdrawal of sample solutions. Five ml. of sample solutions were drawn out at desired time intervals with dry pipettes to record the progress of the reaction and the volume withdrawn was compensated with distilled water having required concentration of sulphuric acid. A narrow polythene tubing about \( \frac{1}{2} \)" long having sintered glass disc at one end was attached to the tip of the pipette in order to prevent sucking out any mineral particles. The volume of each sucked out solution was then made 50 ml. Ferrous iron in the withdrawn solutions was then determined by titrating an aliquot against standard potassium dichromate solution in the presence of phosphoric acid using barium diphenyl amine sulphonate as indicator. Total iron was determined by titrating in the same way after stannous chloride reduction.

Manganese in the same solution was determined by titrating an aliquot against EDTA at pH 10 (\( \text{NH}_4\text{OH-NH}_4\text{Cl} \) buffer) in the presence of hydroxylamine hydrochloride and triethanolamine using thymolphthalxone as the indicator. Sometimes sulphate was determined only for checking of analyses values by interacting an aliquot of sample solution with known strength and volume of
Barium chloride solution in excess and titrating the excess Barium chloride with standard sodium sulphate solution using sodium rhodizonate as indicator\(^{120}\).

Some leached residues were analysed for basic sulphate and elemental sulphur as per the following procedure. After carrying out the reaction for desired period the container was opened and the contents were filtered through a previously weighed sintered glass crucible. The residue was thoroughly washed with warm water in order to make the residue free of sulphate. Finally, it was washed with absolute alcohol and vacuum dried at about 50\(^\circ\)C in order to avoid volatilisation of elemental sulphur. The residue was then treated with hot toluene which dissolved in sulphur and after filtration, the loss in weight of the residue gave the amount of sulphur. Then the residue was treated with 2N hydrochloric acid, filtered and thoroughly washed with water. Sulphate was determined in the filtrate as mentioned above and noted as basic sulphate.

4.1.2 ELECTROCHEMICAL STUDIES:

4.1.2.1 Preparation of Electrodes:

The samples used in this investigation for making the electrodes include synthetic \(\beta\)-MnO\(_2\) and high grade crystalline pyrite. For electrode preparation,
5g of $\beta$-MnO$_2$ or crystalline pyrite sample was mixed thoroughly with 1g graphite and 0.6g of transoptic powder (Buehler Ltd., USA make). Graphite was used to increase the conductivity of the pellet and transoptic powder was used as a binder. The mixture was kept in a cylindrical stainless steel mould of diameter 1 inch. The material was compacted by means of a plunger (Buehler Ltd., USA, Simpliment II) that fitted the sample cavity exactly and a load of 5000 lb/inch$^2$ was applied for 30 minutes. During compression, the mould was kept at a temperature of 130±5°C. Then one conducting wire was attached to one plane face of compressed pellet with the help of a silver based conducting cement. The ohmic contact was checked up and then the pellet was mounted in araldite keeping the other plane face open.

Before starting experiments the open face of each electrode was hand polished each time with emery papers of grade 400, 600, 800 and with filter paper, washed with distilled water and acetone and kept in a vacuum desiccator.

4.1.2.2 Preparation of electrolyte:

Distilled water and reagent grade H$_2$SO$_4$ were used to prepare 0.2M H$_2$SO$_4$. Reagent grade FeSO$_4$.$H_2$O
and Fe$_2$(SO$_4$)$_3$ were used wherever Fe$^{2+}$ and Fe$^{3+}$ ions were needed.

4.1.2.3 Measurement of Electrochemical Parameters in dual Cell:

Electrochemical parameters like potential, galvanic current were measured using a dual cell as shown in Fig. 4.2. It was a two compartment apparatus, each side being separated by a membrane (cation 61AZL389 made by Ionics incorporated, Water town, Mass) which allowed the flow of electrons through it but not that of ions. The circuit consists of a polished pyrite electrode in one compartment and a polished $\beta$ -MnO$_2$ electrode in the other, connected externally through a variable resistance and microammeter. Each electrode was connected to a standard calomel electrode (SCE) through a microvoltmeter. The calomel electrode was internally connected through a salt bridge. Each compartment was filled with 500 ml of required electrolyte. Stirring of solution in each compartment was done by one glass impeller attached to a 1/12 HP motor. Rest potentials of each of the electrodes of the couple were noted with resistance full and microammeter reading zero. Then by externally varying the resistance stepwise from an infinitely high value (open circuit) down to zero (the mixed potential, $E_m$), each half cell steady
Fig. 4.2 Schematic diagram of the experimental setup used for electrochemical measurements in dual cell.
state potential (with one minute holding) and the current were recorded. These data enabled to plot Evans diagram. In the present study all the potentials measured were in millivolts (mv) versus SCE and galvanic current values were expressed in microampers (mAmp) per total area of electrode (0.7854 inch\(^2\)).

4.1.2.4 Pellet leaching study in dual cell:

Leaching studies were conducted using the same electrodes and dual cell set up. The first 120 minutes of leaching was conducted to record individual mineral dissolution after which the electrodes were externally connected to record galvanic dissolution. Five ml. of sample solutions were drawn from each compartment at required intervals. The solutions were analysed for manganese and iron by Atomic Absorption Spectrophotometer in order to assess the dissolution rates of manganese and iron into the solution.

4.1.2.5 Galvanostatic polarisation curve:

Galvanostatic polarization curves were plotted for each electrode and \( \text{Fe}^{++}/\text{Fe}^{+++} \) couple using model 362 scanning potentiostat of EG&G PARC coupled with series 2000 Omnigraphic X-Y recorder of Houston Instruments Division. Platinum (inert) electrode was taken
in place of manganese dioxide or pyrite electrode to record the corrosion curves for Fe$^{+\text{+}}$/Fe$^{\text{+++}}$ couple.

4.2 RESULTS AND DISCUSSION:

4.2.1 Suspended particle leaching of pyrite in 0.2N H$_2$SO$_4$:

Suspended particle leaching experiments were carried out to study the leaching behaviour of pyrite in 0.2N H$_2$SO$_4$. 2.7 gm of crystalline pyrite was agitated at the rate of 600 minute$^{-1}$ in 1500 ml of 0.2N H$_2$SO$_4$. Temperature of the slurry was maintained at 100°C. The values of Fe$^{+\text{+}}$ and total iron recovery into the solution are presented in Table 4.1. It is observed from the table that the total iron recovery in 15 minutes was 35.2% and there was no further increase with time till 120 minutes. This dissolution is supposed due to the oxidation of pyrite by atmospheric oxygen as reported by Thomas and Walley$^{41}$. They reported the following stoichiometry for aqueous oxidation of pyrite.

$$\text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} \longrightarrow \text{FeS}_\text{O}_4 + \text{H}_2\text{SO}_4 \quad (4.1)$$

4.2.2 Suspended particle leaching of $\beta$-MnO$_2$ in 0.2N H$_2$SO$_4$:

MnO$_2$ was leached in 1500 ml of 0.2N H$_2$SO$_4$ at the temperature of 100°C and agitation rate of 600 minute$^{-1}$. Dissolution data of manganese are presented
### TABLE - 4.1

Iron dissolution in suspended particle leaching of crystalline pyrite in 0.2N \( \text{H}_2\text{SO}_4 \). Crystalline Pyrite - 2.7 gm, 0.2N \( \text{H}_2\text{SO}_4 \) - 1500ml, Temp. -100°C, Agitation - 600 min^{-1}

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Fe^{++} dissolution</th>
<th>Total Fe dissolution %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>19.6</td>
<td>23.5</td>
</tr>
<tr>
<td>10</td>
<td>27.4</td>
<td>29.2</td>
</tr>
<tr>
<td>15</td>
<td>31.3</td>
<td>35.2</td>
</tr>
<tr>
<td>30</td>
<td>35.2</td>
<td>39.1</td>
</tr>
<tr>
<td>45</td>
<td>35.2</td>
<td>39.1</td>
</tr>
<tr>
<td>60</td>
<td>35.2</td>
<td>37.1</td>
</tr>
<tr>
<td>90</td>
<td>35.2</td>
<td>37.1</td>
</tr>
<tr>
<td>105</td>
<td>35.2</td>
<td>35.2</td>
</tr>
<tr>
<td>120</td>
<td>33.2</td>
<td>35.2</td>
</tr>
</tbody>
</table>

### TABLE - 4.2

Manganese dissolution in suspended particle leaching of \( \beta\)-\( \text{MnO}_2 \) in 0.2N \( \text{H}_2\text{SO}_4 \). \( \beta\)-\( \text{MnO}_2 \) - 3 gms. 0.2N \( \text{H}_2\text{SO}_4 \) - 1500 ml Temperature - 100°C, Agitation - 600 min^{-1}

<table>
<thead>
<tr>
<th>Time in minute</th>
<th>Mn dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.03</td>
</tr>
<tr>
<td>10</td>
<td>3.03</td>
</tr>
<tr>
<td>15</td>
<td>3.03</td>
</tr>
<tr>
<td>30</td>
<td>3.03</td>
</tr>
<tr>
<td>60</td>
<td>3.03</td>
</tr>
<tr>
<td>120</td>
<td>3.03</td>
</tr>
</tbody>
</table>
in Table-4.2. Manganese dissolution was 3.93% at 5 minutes which did not rise further till 120 minutes. This low recovery of manganese is obvious because pure manganese dioxide does not dissolve in dilute sulphuric acid except in the presence of reducing agents. The dissolution of small quantity of manganese may be due to the presence of some Mn^{++} and Mn^{+++} in the \( \beta \)-MnO\(_2\) sample.

In the next experiment suspended particle leaching was conducted for the mixture of \( \beta \)-MnO\(_2\) and pyrite.

4.2.3 Leaching of \( \beta \)-MnO\(_2\) and Pyrite mixture in 0.2N H\(_2\)SO\(_4\):

3 gms of \( \beta \)-MnO\(_2\) and 2.7 gms of crystalline pyrite were mixed together and agitated at 600 minute\(^{-1}\) in 1500 ml of 0.2N H\(_2\)SO\(_4\). The temperature was kept at 100°C. The results presented in Fig. 4.3 reveal that recovery of iron in the combined leaching is higher than the same in the leaching of pyrite alone (Table 4.1). Manganese recovery of combined leaching is also higher than the corresponding manganese leaching from \( \beta \)-MnO\(_2\) alone (Table 4.2). The higher dissolution of manganese and iron in the combined suspended particle leaching may be due to two reasons. In reason 1 the species Fe\(^{++}\) generated by oxidation of FeS\(_2\) (Equation-4.1) reduces MnO\(_2\) to Mn\(^{++}\). The stoichiometry of reduction
Dissolution of manganese and iron from $\beta$-MnO$_2$ and crystalline pyrite mixture in suspended particle leaching.
of MnO$_2$ by FeSO$_4$ in H$_2$SO$_4$ medium as reported by Levan et al.\textsuperscript{107} and also Cornelius & Woodcock\textsuperscript{112} is as follows:

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

or,

\[ \text{MnO}_2 + 2\text{Fe}^{++} + 4\text{H}^{+} \rightarrow \text{Mn}^{++} + 2\text{Fe}^{+++} + 2\text{H}_2\text{O} \] (4.2)

In the combined leaching Fe$_2$(SO$_4$)$_3$ generated as in eqn. 4.2 oxidises pyrite generating ferrous ion. Thomas and Walley\textsuperscript{41} studied the leaching of pyrite with ferric sulphate solutions and proposed the following stoichiometry (Eqn. 4.3):

\[ \text{FeS}_2 + 7\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O} \rightarrow 15 \text{FeSO}_4 + 8\text{H}_2\text{SO}_4 \] (4.3)

There may be also a side reaction (Eqn. 4.4) forming elemental sulphur as reported by Rath et al.\textsuperscript{44}.

\[ \text{FeS}_2 + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+} + 2\text{S}^0 \] (4.4)

Thus, there is a cyclic generation of Fe$^{2+}$ and Fe$^{3+}$ ions and side by side there is increase in manganese and iron leaching.

Reason II for higher leaching of manganese and iron in the combined leaching may probably be due to galvanic interaction between MnO$_2$ and FeS$_2$ since
both of these species are semiconductors in nature and they readily conduct current. Rest potentials of $\beta$-MnO$_2$ is $+1.23$V SHE and that of pyrite is $+0.63$V SHE. Galvanic interaction cannot be avoided during combined leaching because a good part of the particles may come into contact with each other to form galvanic couples. In order to establish the exact mechanism of the leaching, studies have been conducted to investigate both chemical as well as electro-chemical parameters of the system.

First of all, the effect of different parameters like rate of agitation, reagent concentration, temperature and particle size on suspended particle leaching of manganese dioxide were investigated. Unless otherwise mentioned reaction variables were fixed for the suspended particle leaching as follows:

Leaching solution - 150 ml, $H_2SO_4$ concentration - 0.1N, Manganese ore of -90+75/$\mu$m size - 10g., Shaly pyrite of -90+75/$\mu$m size to make Mn:S atomic ratio - 1:1, agitation rate - 600 min$^{-1}$ and oxygen flow rate - 50 ml/minute.

4.2.4 Effect of agitation rate:

It is well known that a critical stirring rate is required for complete off bottom suspension of
Fig. 4.4 Effect of agitation rate on Mn(II) formation in suspended particle leaching of manganese ore with shaly pyrite.

- Manganese ore - 10 gms
- 0.05M H₂SO₄ - 1500 ml
- Mn:S = 1:1
- Temp. - 100°C

![Graph showing the effect of agitation rate on Mn(II) formation.](image-url)
particles in a liquid medium and that below this critical speed the total surface area of particles is not available for reaction. So rate experiments which aim to discriminate between a diffusion controlled rate model and a chemically controlled one have to be conducted at stirring speeds above this critical value. It has been seen experimentally that at an agitation speed of 300 min\(^{-1}\), a complete off bottom suspension of particles is attained for above size of particles. So four experiments were carried out at agitation speeds of 300 min\(^{-1}\) to 600 min\(^{-1}\). Manganese leaching values are presented in Fig. 4.4 upto 30 minutes. The change in the formation of MnSO\(_4\) with increase in speed of agitation is negligible which precludes diffusion phenomena.

4.2.5 Effect of Oxygen Flow Rate:

Eventhough atmospheric oxygen is available to the system in the present set up of leaching, this study has been carried out in order to assess the effect of oxygen at higher partial pressures. Experiments were carried out varying oxygen flow rate from 0 to 100 ml/minute and the results were presented in Fig. 4.5. In the present system molecular oxygen flow rate upto 50 ml/minute has no significant effect whereas increasing
Fig. 4.5 Effect of Oxygen flow rate on Mn(II) formation in suspended particle leaching of manganese ore with shaly pyrite.
beyond this level is detrimental. This matches with the observation of Dixit and Raisoni\textsuperscript{102} that higher partial pressure of oxygen shifts the oxidation potential of solution to a higher value and inhibits the reduction of MnO\textsubscript{2}.

4.2.6 Effect of acid concentration:

The effect of initial H\textsubscript{2}SO\textsubscript{4} concentration of the solution on manganese dioxide dissociation rate is presented in Fig. 4.6. Dissolution experiments were carried out in the range of 0.01N to 0.2N H\textsubscript{2}SO\textsubscript{4} concentration (pH 2.0 to 0.7). The dependence of $1 - (1-\alpha)^3$ on time indicated the reaction to be following a shrinking core model. The increase of initial concentration of H\textsubscript{2}SO\textsubscript{4} causes distinct increase in rate of dissolution. The plot of log K vs. pH is linear with a negative slope of 0.25 (Figure-4.7) so that the order of the reaction with reference to pH is -0.25.

Fe\textsuperscript{++} and Fe\textsuperscript{+++} contents of leaching solutions are given in Table-4.3. In 0.01N H\textsubscript{2}SO\textsubscript{4} dissolution of iron is very low. Fe\textsuperscript{2+} content is slightly increasing with time but Fe\textsuperscript{3+} becomes nil in the final solution. In 0.5N H\textsubscript{2}SO\textsubscript{4}, initial Fe\textsuperscript{2+} quantity is high which gradually decreases with time. Fe\textsuperscript{3+} quantity increases upto 15
Fig. 4.6 Plot of $[1 - (1-\alpha)^{1/3}]$ Vs. time for Mn(II) formation in suspended particle leaching of manganese ore with shaly pyrite at different acid concentrations.

Size: $90 + 75 \mu m$
Temp: $100^\circ C$
600 min$^{-1}$
Manganese ore: $10 g$
Mn:S = 1:1
Leaching solution: $1500 ml$

H$_2$SO$_4$
- $0.005 M$
- $0.025 M$
- $0.050 M$
- $0.100 M$
Fig. 4.7 Plot of pH Vs. Log K for Mn(II) formation in suspended particle leaching of manganese ore with shaly pyrite.

- SIZE: 90 + 75 μm
- Temp.: 100 °C
- Manganese ore: 10 g
- 600 min⁻¹
- Mn : S = 1 : 1
- Leaching solution: 1500 ml
Table 4.3 Effect of $\text{H}_2\text{SO}_4$ Concentration on Suspended particle leaching of Manganese Ore and Shaly Pyrite mixture.

<table>
<thead>
<tr>
<th>Time in minute</th>
<th>0.25 M $\text{H}_2\text{SO}_4$</th>
<th>0.05M $\text{H}_2\text{SO}_4$</th>
<th>0.1 M $\text{H}_2\text{SO}_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn.g mole $\times 10^3$</td>
<td>Mn.recovery %</td>
<td>Total Fe.g mole $\times 10^3$</td>
</tr>
<tr>
<td>5</td>
<td>12.63</td>
<td>17.90</td>
<td>5.24</td>
</tr>
<tr>
<td>10</td>
<td>17.36</td>
<td>24.60</td>
<td>5.24</td>
</tr>
<tr>
<td>15</td>
<td>25.21</td>
<td>35.72</td>
<td>5.24</td>
</tr>
<tr>
<td>20</td>
<td>28.40</td>
<td>40.24</td>
<td>4.49</td>
</tr>
<tr>
<td>25</td>
<td>32.32</td>
<td>45.80</td>
<td>3.00</td>
</tr>
<tr>
<td>30</td>
<td>37.64</td>
<td>53.61</td>
<td>2.25</td>
</tr>
<tr>
<td>45</td>
<td>42.56</td>
<td>60.30</td>
<td>1.13</td>
</tr>
<tr>
<td>60</td>
<td>48.84</td>
<td>69.20</td>
<td>1.13</td>
</tr>
<tr>
<td>75</td>
<td>51.25</td>
<td>72.62</td>
<td>0.75</td>
</tr>
<tr>
<td>90</td>
<td>52.79</td>
<td>74.80</td>
<td>0.75</td>
</tr>
<tr>
<td>105</td>
<td>55.19</td>
<td>78.20</td>
<td>0.75</td>
</tr>
</tbody>
</table>
minutes, then decreases to nil. In 0.1N H₂SO₄ initial Fe³⁺ quantity is high. It attains the highest at 15 minutes and then decreased gradually to zero. Fe²⁺ quantity increases with time upto the end of the experiment. Initial high quantity of Fe³⁺ ion indicates that in 0.1N H₂SO₄, Fe³⁺ forming (Fe²⁺ consuming) reaction step is very fast. In 0.2N H₂SO₄, Fe²⁺ quantity increases upto the end of the experiment, Fe³⁺ quantity increases upto 45 minutes and then it decreases. In general, total iron quantity increases with increase of H₂SO₄ concentration. This implies that perhaps ferrous iron gets consumed immediately as it forms till the other reactant (MnO₂) consuming ferrous iron is practically exhausted. Subsequently, Fe³⁺ builds up slowly at the expense of Fe⁴⁺. That means reaction (4.2) and (4.3) proceed simultaneously, the former being faster till MnO₂ is exhausted and subsequently, only reaction (4.3) proceeds. Ferric ion precipitates out at low [H⁺]. Mn and total Fe recoveries as well as ferrous concentration reported in Table 4.3 support this idea. In H₂SO₄ of 0.05N or below total iron quantity decreases with time because of the precipitation of ferric hydroxide.

Residues of suspended particle leaching experiments at different H₂SO₄ concentrations were analysed
for basic sulphate and elemental sulphur contents and the data were presented in Table 4.4. The data reveal that leaching with high sulphuric acid concentration

**TABLE - 4.4**

Formation of basic sulphate and sulphur with different initial sulfuric acid concentrations in suspended particle leaching.

Leaching solution - 1500 ml, Temp. -100°C, Time - 2h., MnO$_2$ - 0.07058 g. mole, FeS$_2$ - 0.03529 g. mole

<table>
<thead>
<tr>
<th>Initial H$_2$SO$_4$ g.mole</th>
<th>FeSO$_4$ in solution g.mole</th>
<th>Fe$_2$(SO$_4$)$_3$ in solution g.mole</th>
<th>MnSO$_4$ in solution g.mole</th>
<th>Basic sulphate in residue g.mole</th>
<th>Elemental sulphur in residue g.mole</th>
<th>Basic elemental molar ratio of S and pyrite oxidised</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0375</td>
<td>0.00075</td>
<td>0</td>
<td>0.05519</td>
<td>0.0252</td>
<td>0.0021</td>
<td>0.0809</td>
</tr>
<tr>
<td>0.075</td>
<td>0.00675</td>
<td>0</td>
<td>0.06468</td>
<td>0.0113</td>
<td>0.0037</td>
<td>0.2049</td>
</tr>
<tr>
<td>0.15</td>
<td>0.02175</td>
<td>0.00525</td>
<td>0.07054</td>
<td>0.0005</td>
<td>0.0085</td>
<td>0.2595</td>
</tr>
</tbody>
</table>

favours the sulphur forming reaction and at low acid concentration sulphur formation is very very low. Basic sulphate precipitates in the residue at low acid concentration. Last column of table 4.4 presents the molar ratio of elemental sulphur formed and total pyrite oxidised. The ratio are about 0.08, 0.20 and 0.26 in 0.5N, 0.1N and 0.2N H$_2$SO$_4$ respectively.
4.2.7 Effect of Pyrite Concentration:

Measurements were carried out varying S:Mn atomal ratio within 1 to 3 by changing pyrite quantity and fixing the quantity of manganese ore at 10 gms. The increase of initial concentration of pyrite causes a distinct increase in manganese dissolution rate (K) (Fig. 4.8). The plot of log K vs. log [pyrite] mole/L was a straight line with a slope of 0.66 (Fig. 4.9). So the reaction order with reference to pyrite concentration was determined as 0.66.

Fe$^{++}$ and Fe$^{+++}$ ion concentration in the leaching solution increases with increase of pyrite to MnO$_2$ ratio in the pulp (Table-4.5). Always Fe$^{++}$ concentration increases with time whereas Fe$^{+++}$ concentration increases to reach a maximum and then it decreases with time. This again implies that both reactions (4.2 and 4.3) proceed simultaneously till MnO$_2$ gets exhausted and then reaction (4.3) proceeds alone.

4.2.8 Effect of Temperature:

Suspended particle leaching experiments of manganese ore and pyrite mixtures were conducted at 40°C, 60°C, 80°C and 100°C. The time dependance of extraction of manganese was shown in (Fig. 4.10). Plots
Fig. 4.8  Plot of $[1-(1-\alpha)^{1/3}]$ Vs. time for Mn(II) formation in suspended particle leaching of manganese ore with different concentrations of shaly pyrite.
Fig. 4.9 Plot of Log $k_{\text{min}}$ Vs. Log (Pyrite) for Mn(II) formation in suspended particle leaching of manganese ore with shaly pyrite.

Manganese ore - 10 g
H$_2$SO$_4$ 0.05 M - 1500 ml
Temp. 100°C
600 min$^{-1}$
Table 4.5 Effect of Pyrite Concentration on Suspended particle leaching of Manganese Ore and Shely Pyrite Mixture

Mn in the Manganese Ore taken - 0.07058 gm-mole
0.1 N H$_2$SO$_4$ - 1500 ml, Temperature - 100°C

<table>
<thead>
<tr>
<th>Time in minute</th>
<th>$\text{FeS}_2 = 0.03529$ gm-mole</th>
<th>$\text{FeS}_2 = 0.07058$ gm-mole</th>
<th>$\text{FeS}_2 = 0.10587$ gm-mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn extracted g.mole x 10$^3$</td>
<td>Mn recovery %</td>
<td>Total Fe extracted g.mole x 10$^3$</td>
</tr>
<tr>
<td>5</td>
<td>13.42</td>
<td>19.01</td>
<td>7.50</td>
</tr>
<tr>
<td>10</td>
<td>21.25</td>
<td>30.12</td>
<td>9.00</td>
</tr>
<tr>
<td>15</td>
<td>26.84</td>
<td>38.08</td>
<td>9.00</td>
</tr>
<tr>
<td>20</td>
<td>33.88</td>
<td>48.01</td>
<td>9.00</td>
</tr>
<tr>
<td>25</td>
<td>39.38</td>
<td>55.80</td>
<td>9.00</td>
</tr>
<tr>
<td>30</td>
<td>48.35</td>
<td>61.42</td>
<td>9.00</td>
</tr>
<tr>
<td>45</td>
<td>54.36</td>
<td>77.03</td>
<td>8.25</td>
</tr>
<tr>
<td>60</td>
<td>69.10</td>
<td>83.74</td>
<td>7.50</td>
</tr>
<tr>
<td>75</td>
<td>66.15</td>
<td>87.14</td>
<td>6.75</td>
</tr>
<tr>
<td>90</td>
<td>64.26</td>
<td>91.05</td>
<td>6.75</td>
</tr>
<tr>
<td>105</td>
<td>64.68</td>
<td>91.65</td>
<td>6.75</td>
</tr>
</tbody>
</table>
Fig. 4.10 Effect of temperature on Mn (II) formation in suspended particle leaching of manganese ore with shaly pyrite.
Fig. 4.11 Plot of \([1-(1-\alpha)^{1/3}]\) Vs. time for Mn(II) formation in suspended particle leaching of manganese ore with pyrite at different temperature.

- Size: 90 + 75 μm
- 600 min\(^{-1}\)
- H\(_2\)SO\(_4\) 0.05M - 1500 ml
- Manganese ore: 10 g
- Mn : S = 1:1
Fig. 4.12 Arrhenius plot for Mn(II) formation in suspended particle leaching of manganese ore with shaly pyrite.
Fig. 4.13 Plot of Log \( \frac{K}{T} \) Vs. \( \frac{1}{T} \) for Mn (II) formation in suspended particle leaching of manganese ore with shaly pyrite.
of \(1 - (1 - \alpha)^\frac{b}{b}\) vs. time were shown in Fig. 4.11. The Arrhenius plots were given in Figs. 4.12 and 4.13. The apparent activation energy \(\Delta E\) and enthalpy of activation, \(\Delta H\) were calculated using standard equations 4.5 and 4.6 and found 43.61 KJ/mole and 41.25 KJ/mole, respectively.

\[
\log K = \frac{\Delta E}{2.303 \ RT} + \log A
\] (4.5)

\[
\log K/\ T = \frac{\Delta H}{2.303 \ RT} + \log \left[ \frac{K}{h} \ exp \left( \frac{\Delta S}{R} \right) \right]
\] (4.6)

where, \(A\) = Pre-expotential frequency factor (L mol\(^{-1}\) s\(^{-1}\))

\(S\) = entropy of activation (J mol\(^{-1}\) K\(^{-1}\))

\(R\) = Gas constant (8.3144 J mol\(^{-1}\) K\(^{-1}\))

\(K\) = Boltzman constant (1.380 \times 10^{-23}; \ K^{-1})

\(h\) = Plank's constant (6.625 \times 10^{-34}; \ Js)

and \(T\) = Temperature (°K)

This level of activation energy suggests probable surface reaction controls the process.

4.2.9 Effect of Particle size and Surface Area:

The effect of surface area on leaching was studied by determining the rate of dissolution of 4 size fractions of manganese ore (Fig. 4.14). The rate of dissolution was found to be increased with increase of surface area.
Fig. 4.14 Effect of particle size of manganese ore on Mn (II) formation in suspended particle leaching with shaly pyrite.
For spherical particles the following relationship between fraction reacted \((\alpha\) ) and time \((t)\) is well established : 

\[
\frac{d\alpha}{dt} = \frac{6(b/a)M_{\text{MnO}_2}}{p_{\text{MnO}_2}d_0}\frac{K[\text{Pyrite}]}{n[1-(1-\alpha)^{\frac{1}{n}}]} \tag{4.7}
\]

Where \(K\) - reaction rate constant (cm/min for \(n=1\)), \(n\) = order of reaction, \(d_0\)=initial particle diameter (cm), \(p_{\text{MnO}_2}\) = density of MnO\(_2\) (g K\(^{-3}\)), \(M_{\text{MnO}_2}\) = Molecular weight of MnO\(_2\) (g/mol), \(b/a\) = stoichiometric factor (moles of FeS\(_2\) for mole of MnO\(_2\)) and \([\text{pyrite}]\) = concentration of total pyrite (mol/L). Integration of the rate equation indicates that a plot of \((1-(1-\alpha)^{\frac{1}{n}})\) vs. time should be linear provided pyrite is in excess, such is the case for experimental data presented in Figure 4.14. Further, the different slopes should be indicative of the inverse first-order relationship between the reaction rate and initial particle diameter. Figure 4.15 confirms this linear relationship with extrapolation through the origin. Also in the Figure-4.15 the plot of surface area (m\(^2\)/g) vs. rate (K) is seen to be linear. This again supports the idea of a surface reaction controlled process.

These studies so far has indicated that the process is perhaps, surface reaction controlled. Two
Fig. 4.15 Plot of $1/d_0$ Vs. rate for Mn(II) formation in suspended particle leaching of manganese ore with shaly pyrite.

Surface area, m²/g

$\text{Mn : S = 1:1}$
$\text{H}_2\text{SO}_4 \ 0.05 \text{M} - 1500 \text{ml}$

Manganese ore - 10g
$600 \text{ min}^{-1}$
Temp. 100°C

$k \times 10^{-3}, \text{min}^{-1}$

$d_0^{-1}, \text{cm}$
reactions (4.2) and (4.3) might be proceeding simultaneously with the former at a faster rate till MnO₂ gets exhausted and then reaction (4.3) is the only process. Reaction orders of -0.25 and 0.66 with reference to pH and FeS₂ concentration respectively and activation energy of 43.4 KJ/mole have emerged from these studies.

4.2.10 Galvanic study in dual cell:

It is known that both MnO₂ are semiconductors and galvanic interactions are possible. So some electrochemical measurements were made to evaluate this aspect.

Electrochemical parameters like rest and mixed potentials and galvanic current were measured with the help of the dual cell using both MnO₂ and FeS₂ as two corroding electrodes. Finally the Evan's diagram was plotted which helped to know the rate controlling step of this electrochemical reaction. The values of $i_{corr.}$ for pyrite and $\beta$-MnO₂ and the value of $i_{galvanic}$ were also compared with dissolution rates of manganese and iron, conducting leaching studies with the same electrodes in similar conditions.

The rest potentials of pyrite and $\beta$-MnO₂ were measured to be +390 mV and +849 mV respectively against
standard calomel electrode. The values obtained for MnO₂ differ to some extent from the standard values which may be due to impurities. The values indicate that β-MnO₂ is cathodic to pyrite and the difference of their rest potentials is good enough for a galvanic interaction to take place between them. The Evan's diagram for this couple obtained from the dual cell measurements is plotted in Figure 4.16. This gives a mixed potential value of +725 mV, galvanic current of 8400/\text{A}, corrosion current of 330/\text{A} for anodic process and corrosion current of 1480/\text{A} for cathodic process. The galvanic current is 25.5 times of that of the (i\text{corr}) of pyrite and 5.8 times of that of the (i\text{corr}) of β-MnO₂. This indicates that the galvanic interaction predominates over each individual corrosion process. This also indicates that the free corrosion rate of manganese is about 4.4 times of that of the free corrosion rate of pyrite. This aspect will be further discussed when these values will be compared with experimental leaching data in the next section.

The mixed potential of the couple lies closer to the cathodic rest potential than anodic potential, i.e., 124 mVs away from cathodic and 459 mVs from anodic. This indicates a sluggish anodic process. Thus, anodic
Fig. 4.16 Evan's diagram for electrochemical interaction between $\beta$-MnO$_2$ and pyrite electrodes in 0.1 M H$_2$SO$_4$, Temp. 30°C.
process of pyrite is the probable rate controlling step in this galvanic interaction.

4.2.11 Leaching study of MnO₂ and pyrite electrodes:

Baily and Peters⁴⁸ and also Biegler and Swift⁵¹ reported that pyrite reacts with water at an anodic site as per equation (4.8):

\[ \text{FeS}_2 + 8\text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 16\text{H}^+ + 15\text{e}^- \] (4.8)

At cathodic site oxygen is reduced to water as per the reaction (4.9).

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \] (4.9)

On the other hand, Miller and Wan¹⁰⁴ reported the stoichiometry for cathodic half-cell reaction of dissolution of MnO₂ in acid solution as:

\[ \text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \] (4.10)

In the present work for galvanic interaction of pyrite with MnO₂, equation 4.8 and equation 4.10 are assumed to be the reactions at anodic and cathodic sites, respectively. Thus, the cell reaction for the whole process comes out as equation 4.11.
2[FeS₂ + 8H₂O → Fe³⁺ + 2SO₄²⁻ + 16H⁺ + 15e⁻] (4.8)  
15[MnO₂ + 4H⁺ + 2e⁻ → Mn²⁺ + 2H₂O] (4.10)  

2FeS₂ + 15MnO₂ + 28H⁺ → 2Fe³⁺ + 15Mn²⁺ + 4SO₄²⁻ + 14H₂O (4.11)

According to equation 4.11, one molecule of FeS₂ can reduce 7.5 molecules of MnO₂ during galvanic interaction.

Leaching studies of the β-MnO₂ electrode and pyrite electrode have been carried out using the same apparatus and the same leaching conditions for generating the data that is necessary to compare with galvanic measurements. Dissolution rates of manganese and iron into the solution were measured by determining the manganese and iron quantities in the time to time drawn out solutions by atomic absorption spectrophotometer. Free corrosion was studied for 120 minutes, then the two electrodes were externally connected in order to obtain the galvanic dissolution rates. These dissolution rates have been converted to the current equivalent applying Faraday's law with an assumption that this would have been corrosion current (galvanic current in case of couple) if 100 pct dissolution takes place as per corrosion or galvanic principles and following
the half cell reactions, 4.8 and 4.10. Dissolution data of iron and manganese are presented in Figure 4.17. The plots of dissolution of iron and manganese versus time are linear with low slope values upto 120 minutes when each was dissolving independently. After connection, the plots have much higher slope values. Iron dissolution plot before connection gives a slope of $0.0111$ gm/sec., which is equivalent to a $i_{corr}$ value of $288$ $\mu$A. Likewise slope of the plot of Free Corrosion of Manganese is found to be $0.403$ gm/sec. and $i_{corr}$ for manganese is calculated to be $1415$ $\mu$A. Here the corrosion rate of manganese is $4.9$ times of that of iron. These observation is in good agreement with the observation made in the Evan's diagram (Fig.4.16). After connection of electrodes the plot for dissolution of iron gives a slope of $0.2687$ gm/sec., equivalent of $6965$ $\mu$A. Plot of manganese dissolution after connection gives a slope of $2.42$ gm/sec. which after converting to current gives $i_{galvanic}$ equal to $8489$ $\mu$A. All these parameters are listed in Table 4.6. It can be observed from the table that notwithstanding the difference in galvanic current obtained from dissolution of iron and manganese these values can be considered to match well with those obtained from the galvanic measurement.
Fig. 4.17 Open and closed circuit dissolution of manganese dioxide and pyrite electrodes in 0.1 M H$_2$SO$_4$. 
The low values obtained from long leaching studies in comparison to those obtained from dual cell are obviously due to some surface coverage emerging from long exposure. But the general trend is crystal clear. So it may be inferred that galvanic interaction is taking place between pyrite and MnO₂ according to the half cell reactions 4.8 and 4.10. But in the slurry leaching the extent of coupling, possible in the vessel is an unknown quantity and moreover the probability of chemical route through reaction 4.2 always exist. In order to investigate this aspect, one slurry leaching was conducted in 0.2N orthophosphoric acid solution instead of 0.2N H₂SO₄ solution. It was assumed that orthophosphoric acid would combine with Fe³⁺ ion produced in the cycle of chemical reactions (eqn. 4.2 and 4.3) and hence, blocks the Fe²⁺ production. Galvanic interaction would be the only route for leaching of iron and manganese.

**TABLE-4.6**

Comparison of Electrochemical and dissolution study measurements for corrosion and galvanic currents of β-MnO₂ and crystalline pyrite dipped in 0.1M H₂SO₄

<table>
<thead>
<tr>
<th>Electrochem Measurements</th>
<th>Dissolution study Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Corr of pyrite MnO₂/Amp</td>
<td>1 Corr of pyrite MnO₂/Amp</td>
</tr>
<tr>
<td>1 Corr of MnO₂/Amp</td>
<td>1 Corr of MnO₂/Amp</td>
</tr>
<tr>
<td>g obtained from Fe/Amp</td>
<td>g obtained from Mn/Amp</td>
</tr>
<tr>
<td>g obtained from Fe/Amp</td>
<td>g obtained from Mn/Amp</td>
</tr>
</tbody>
</table>

| 330 | 1450 | 8400 | 360 | 1415 | 6965 | 8489 |
4.2.12 Leaching study in Orthophosphoric acid:

Slurry leaching was carried out in 0.2N $H_3PO_4$ solution with 3g $\beta$MnO$_2$ and 2.7 gms of crystalline pyrite keeping the temperature at 100°C and agitation speed 600 min$^{-1}$. The leaching results are presented in Table-4.7. Leaching values of iron and manganese are in increasing trend upto 45 minutes. After this period no further dissolution of iron and manganese take place. This may be due to a product layer formation on $\beta$-MnO$_2$. Leaching study in the similar conditions but in 0.2N $H_2SO_4$ was carried out earlier and data were presented in Fig. 4.3. Comparing these results, it has been inferred that galvanic interaction between MnO$_2$ and FeS$_2$ is roughly about 10% of the total manganese dissolution in 0.2N $H_2SO_4$. This may be due to limited contact in the prevailing hydrodynamic conditions and solid concentration. Thus, the major part of the dissolutions are taking place through reactions (4.1), (4.2) and (4.3). Fe$^{+++}$ and Fe$^{++}$ ions appear to have dominating effects on leaching of FeS$_2$ and MnO$_2$.

\begin{align*}
\text{FeS}_2 + \frac{7}{2} O_2 + H_2O &\rightarrow FeSO_4 + H_2SO_4 \quad (4.1) \\
\text{MnO}_2 + 2FeSO_4 + 2H_2SO_4 &\rightarrow MnSO_4 + Fe_2(SO_4)_3 + 2H_2O \quad (4.2) \\
\text{FeS}_2 + 7Fe_2(SO_4)_3 + 8H_2O &\rightarrow 15FeSO_4 + 8H_2SO_4 \quad (4.3)
\end{align*}
Manganese and iron dissolution in suspended particle leaching of $\beta$-MnO$_2$ and crystalline pyrite mixture. 

$\beta$-MnO$_2$ - 3 gms, Crystalline pyrite - 2.7 gm 

$0.2H_3PO_4$ - 1500 ml, Temp. - 100°C

<table>
<thead>
<tr>
<th>Time in minute</th>
<th>Total Fe dissolution %</th>
<th>Manganese dissolution %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>7.80</td>
<td>4.41</td>
</tr>
<tr>
<td>10</td>
<td>8.42</td>
<td>6.52</td>
</tr>
<tr>
<td>15</td>
<td>8.42</td>
<td>6.63</td>
</tr>
<tr>
<td>30</td>
<td>9.45</td>
<td>6.63</td>
</tr>
<tr>
<td>45</td>
<td>9.92</td>
<td>8.71</td>
</tr>
<tr>
<td>60</td>
<td>9.92</td>
<td>8.71</td>
</tr>
<tr>
<td>90</td>
<td>9.92</td>
<td>8.71</td>
</tr>
<tr>
<td>120</td>
<td>9.92</td>
<td>8.71</td>
</tr>
</tbody>
</table>

Iron dissolution data in 0.2N H$_2$SO$_4$ as per Table-4.3 presents the following important observations:

(i) During initial stage Fe$^{+++}$ ion concentration of leach liquor increases, Fe$^{++}$ ion concentration decreases and manganese dissolution increases.

(ii) After 60 minutes, when manganese dissolution gets nearly completed, Fe$^{+++}$ ion concentration declines and Fe$^{++}$ concentration increases.
This implies that Fe\textsuperscript{+++} ion produced through reactions (4.1) and (4.3) gets consumed immediately through reaction (4.2) and the reaction (4.2) is a faster reaction in comparison to the reactions (4.1) and (4.3). After completion of manganese dissolution Fe\textsuperscript{++} ion builds up in expense of Fe\textsuperscript{+++} (reaction 4.3). Here it may be inferred that interaction of FeS\textsubscript{2} with Fe\textsuperscript{+++} ion is the rate controlling step of this slurry leaching process.

Rath et al.\textsuperscript{44} reported that two reactions, (4.3) and (4.4) were taking place simultaneously at a ratio of 2:1 when pyrite was leached with ferric chloride solution:

\[
\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad (4.3)
\]

\[
\text{FeS}_2 + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+} + 2\text{S}^0 \quad (4.4)
\]

In the present system molar ratio of elemental sulphur to total pyrite oxidized in 0.1N H\textsubscript{2}SO\textsubscript{4} is about 0.20. So, in this process, one of the above reactions may be the rate controlling step.

4.2.13 Galvanostatic polarisation curves:

In the slurry leaching (Table-4.3) Fe\textsuperscript{++} concentration in initial stages were 0.00025 to 0.0025 g mole/lit
and Fe+++ concentrations were 0.001 to 0.006 g mole/lit. Corrosion curve records obtained with identical Fe++ and Fe+++ concentrations were presented in the Figure 4.18. It is observed from Fig. 4.18 that the mixed current of MnO₂ and 0.01 g mole/lit. of Fe²⁺ is 1600/μA, and that of FeS₂ and Fe³⁺ ion of concentration 0.01 g mole/lit. is around 100/μA only. At a Fe⁺⁺ concentration of 0.0005 M and Fe+++ concentration of 0.011 M, the mixed currents are 200 and 110/μA with MnO₂ and FeS₂ respectively. This again shows that reduction of MnO₂ with Fe⁺⁺ is a comparatively fast reaction and FeS₂ oxidation with Fe+++ is the rate controlling step. But in case of lower Fe⁺⁺ concentration (about 0.0005 M) both reactions may take place at nearly equal rates.

The Evan's diagram of FeS₂ and Fe+++ (Fig.4.18) further suggests that anodic rest potential is +370 mV, the cathodic rest potential is +400 to +435 mV, whereas the mixed potential is +380 mV for pyrite dissolution. This observation shows that mixed potential is very near to the anodic rest potential, i.e., the mixed potential is attained where the anode is still in equilibrium (steady state). That means,

\[ E_{mix} \approx E_{anodic} \]
Fig. 4.18 - Corrosion curve records for manganese dioxide, pyrite and \( \text{Fe}^{2+}/\text{Fe}^{3+} \) couple.

Anodic and cathodic scan - 10 mV/sec., Temp.- 32°C.

I & II - Anodic and cathodic curves of \( \beta - \text{MnO}_2 \) respectively;
\( \beta - \text{MnO}_2 \) electrode in 0.2 N \( \text{H}_2\text{SO}_4 \).

III & IV - Anodic and cathodic curves of pyrite respectively;
crystalline pyrite sample electrode in 0.2 N \( \text{H}_2\text{SO}_4 \).

V, VI, VII & VIII - Anodic and cathodic curves of \( \text{Fe}^{2+}/\text{Fe}^{3+} \) couple;
V & VI - Platinum electrode in 0.01 M \( \text{Fe}^{2+} \), 0.01 M \( \text{Fe}^{3+} \) and 0.2 N \( \text{H}_2\text{SO}_4 \).
VII & VIII - Platinum electrode in 0.0005 M \( \text{Fe}^{2+} \), 0.011 M \( \text{Fe}^{3+} \) and 0.2 N \( \text{H}_2\text{SO}_4 \).
In case of MnO₂ dissolution at lower Fe⁺⁺⁺ concentrations, E_mix is very close to E_{MnO₂} (about +865 mV), i.e.,

\[ E_{mix} \approx E_{cathodic} \]

Wordsworth¹⁵³ has treated elaborately the leaching behaviour of metal sulphides according to the electrochemical theory for a system like FeS₂ in Fe⁺⁺⁺/Fe⁺⁺ or MnO₂ in Fe⁺⁺⁺/Fe⁺⁺⁺, i.e., a semiconductor metal sulphide/oxide mineral dipped inside a solution containing Fe⁺⁺⁺/Fe⁺⁺ redox couple. Treating it as a corrosion system he has developed rate equations through application of Butler-Volmer equation. Reaction (4.3) can be spilt into anodic and cathodic halves as (4.3a) and (4.3c), respectively.

\[ \text{FeS}_2 + 8\text{H}_2\text{O} \rightarrow \text{Fe}^{+++} + 2\text{SO}_{4}^{--} + 16\text{H}^+ + 14\text{e}^- \quad (4.3a) \]

\[ 14(\text{Fe}^{+++} + \text{e}^- \rightarrow \text{Fe}^{+++} ) \quad (4.3c) \]

Following the treatment of Wordsworth¹⁵³, the final rate equation of reaction 4.3 for the condition of

\[ E_{mix} \approx E_{FeS_2} \]

would be:

\[ - \frac{dn_{FeS_2}}{dt} = A_c \frac{K_c}{K_a} \left( \frac{K_a}{K_c} \right)^\beta \left[ \text{SO}_{4}^{--} \right]^\beta \left[ \text{H}^+ \right]^\beta \quad (4.12) \]
For a value of 0.5 for $\beta$ it should result -0.5 order dependence on concentrations of both $SO_4^{2-}$ and $H^+$. Similarly, the reaction (4.4) can be split into anodic and cathodic halves, (4.4a) and (4.4c) respectively,

$$FeS_2 \rightarrow Fe^{++} + 2S^0 + 2e^- \quad (4.4a)$$

$$2Fe^{+++} + 2e^- \rightarrow 2Fe^{++} \quad (4.4c)$$

and would result the rate equation (4.13) for the condition of $E_{mix} \approx E_{FeS_2}$

$$-\frac{dn_{FeS_2}}{dt} = A_C K_C \left( \frac{K_a}{K_a} \right)^\beta \frac{(Fe^{+++})^\beta}{(Fe^{++})^\beta} \quad (4.13)$$

This would mean a rate dependence of 0.5 and -0.5 on $[Fe^{+++}]$ and $[Fe^{++}]$, respectively.

Similarly, equation 4.2 can be split into (4.2a) and (4.2c):

$$2[Fe^{++} \rightarrow Fe^{+++} + e^-] \quad (4.2a)$$

$$MnO_2 + 4H^+ + e^- \rightarrow Mn^{++} + 2H_2O \quad (4.2c)$$
and would result the rate expression 4.14 for the condition of \( E_{\text{mix}} \approx E_{\text{MnO}_2} \):

\[
\frac{\text{d}n_{\text{MnO}_2}}{\text{d}t} = A_a K_a \left( \frac{K_c}{K_c^0} \right) \frac{[H^+]^\beta}{[Mn^{++}]^\beta}
\]  

(4.14)

This would make a 0.5 and -0.5 order dependence on \( H^+ \) and \( Mn^{++} \) respectively.

The kinetic studies resulted -0.25 and 0.66 order dependence for the rate on pH and FeS\(_2\) concentration respectively. Since utility of FeS\(_2\) in the system is via Fe\(^{+++}\) and Fe\(^{++}\) only, the results of Fig. 4.8 (K values) are replotted in Fig.1.19 against log[Fe\(^{+++}\)] and log[Fe\(^{+++}\)] values obtained from Table-4.5. Fig.4.19 results a Fe\(^{++}\) and Fe\(^{+++}\) dependance of 0.62 and 0.85 respectively. This would indicate a mixed control for the system, i.e., MnO\(_2\) dissolution and FeS\(_2\) dissolution taking place at similar rates. Rate dependence of -0.25 on pH must have been due to the complicated situation of -0.5 dependence of \([H^+]\) in eqn. (4.12), + 0.5 dependence of \([H^+]\) in eqn. (4.14) and the possibility that both the reactions (4.3) and (4.4) are taking place simultaneously, \([Mn^{++}]\) and \([SO_4^{--}]\) dependence have not been studied with chemical kinetic studies.
Fig. 4.19 Plot of LOG K Vs. LOG [Fe$^{2+}$] and LOG [Fe$^{3+}$] for suspended particle leaching of manganese ore and shaly pyrite in 0.1 N sulfuric acid.