Manganese is an essential ingredient in the large scale manufacture of iron and steel. Manganese chemicals find applications in dry cell battery and in other industries. The low grade manganese ores which are the major deposits of the world are suitable neither for the direct production of ferro-manganese nor for dry cell battery and other industries. In view of the future demands, extensive research work is being carried out on low grade manganese resources which have been directed towards the production of ore substitutes. Both physical and chemical methods have been used for this purpose by different investigators. Physical methods include different ore-dressing techniques such as jigging, tabling and magnetic separation to remove the gangue materials whereas by chemical methods the manganese is converted to water soluble compounds like sulphate, chloride or nitrate which can either be electrolysed to produce MnO₂ or evaporated to produce manganese salts. A multiplicity of extractive metallurgical processes have been proposed and investigated
for recovering manganese from low grade oxide ores. The variety and number of processes give rise to questions on their relative merits. Various pyrometallurgical techniques like reduction roasting of oxide ore with ferrous sulphate, $SO_2$, etc., followed by aqueous leaching have been attempted in different parts of the world. Reduction leaching processes using different reducing agents such as ferrous sulphate, $SO_2$ or sulfurous acid are some of the hydrometallurgical routes tried for the extraction of manganese.

Sulphatizing roasting is carried out to make the manganese minerals water soluble and by the same time to insolubilize the iron as hematite or magnetite. A suitable temperature is chosen at which manganese is selectively converted to sulphate by roasting with an active sulphur species in the presence of air and that temperature becomes too high for sulphatization of iron. Manganese can then be separated from iron minerals and gangue by leaching with water. Manganese oxides are very effective adsorbents for sulphur dioxide and sulphatization of manganese ores or oxides is carried out using sulphur dioxide. Sulphur dioxide is usually manufactured from iron pyrites by roasting at high temperature. Manganese dioxide is one of the catalysts used for the oxidation of sulphides to sulphur dioxide.
This observation is applied to study the sulphatization of manganese oxides and ores with pyrites.

A number of hydrometallurgical processes for concentrating or recovering manganese from low grade oxide ores have been developed or proposed over the years. Among these, the acidulated ferrous sulphate method or the pickle liquor process as it is commonly called and aqueous sulphur dioxide process are more common. Natural manganese resources containing lower manganese oxides such as MnO, Mn₂O₃ and Mn₃O₄ are leached with sulfuric acid alone. But the higher valency manganese compounds (Mn. IV) are inert towards sulphuric acid leaching. They require a reducing agent such as sulphurous acid or ferrous sulphate for their leaching. U.S. Bureau of Mines was to investigate factors influencing the use of steel mill waste pickle liquor for leaching of manganese from low grade ores (Eqn. 1.1). A solution of

\[ \text{MnO}_2 + 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \rightarrow \text{MnSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} \] (1.1)

the composition analogous to steel-mill pickle liquor can be produced by reacting pyrite with oxygen in the presence of water as shown in the following equation.

\[ \text{FeS}_2 + 3\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{FeSO}_4 + \text{H}_2\text{SO}_4 \] (1.2)

This observation is applied in aqueous leaching of manganese from manganese oxides using pyrite directly.
as the reducing agent. Further the semiconductivity
of both the species, viz., manganese dioxide and pyrite
and a substantial difference in their rest potentials
in an electrolyte enhance the possibility of a electro-
chemical redox reaction between the two. Even though
sulphatisation roasting as well as reduction leaching
of manganese dioxide with the help of pyrite has been
reported, information on leaching kinetics and detailed
reaction mechanism are not available in the literature.

Literature survey on relevant topics has been
given in the subsequent passages under the following
headings: (i) general characteristics of pyrite,
(ii) thermal oxidation and decomposition of pyrite,
(iii) aqueous oxidation of pyrite, (iv) structural
characteristics of manganese oxide, (v) general chara-
teristics of manganese ore, (vi) reduction roasting
of manganese dioxide, and (vii) reduction leaching
of manganese dioxide.

GENERAL CHARACTERISTICS OF PYRITE:

"Pyrite" is an inclusive term used to describe
metallic sulphides such as iron pyrite (pyrite, FeS₂),
white iron pyrites (Marcasite, FeS₂), Magnetic pyrites
(Pyrrhotite, FeS), Copper pyrites (Chalcopyrite, CuFeS₄)
and tin pyrites (Stannite, CuSnFeS₄). Iron pyrites¹,²,³,
the disulphide of iron is notably non-stoichiometric,
and its composition ranges from $\text{FeS}_{1.94}$ to $\text{FeS}_{2.04}$ even at ordinary temperature with a corresponding variation in physical properties such as specific gravity and electrical conductivity. The mineral iron pyrites was known to ancient scientists and its references can be traced back to 75 A.D. or even 315 B.C. Its principal use in the middle ages was as source of sulphuric acid. Importance of pyrite as a source of sulphuric acid declined with the development of processes using alternate raw materials.

Pyrite is a common sulphide mineral and is present in most massive hydrothermal sulphide bodies and common in hydrothermal veins and replacements of any formation temperature. It is often found as massive aggregates. In sedimentary rocks it often occurs as globular concretions, sometimes of radical fibrous structure and also as secretions in the cavities of shells. Some of the important properties of the mineral pyrite have been discussed by Shuey. On an ionic model pyrite is $\text{Fe}^{2+} (S_2)^{2-}$. The molecule $(S_2)^{2-}$ would have fully occupied $2 \text{p}_{\pi}$ orbitals and an empty antibonding $2 \text{p}_{5\pi}$ orbital. The $\text{Fe}^{2+}$ ion has the configuration $(3d)^6$. In the high spin state, there are four unpaired spins and hence, a net magnetic moment. But in pyrite, the effective permanent molecular movement is zero.
Evidently, then Fe$^{2+}$ is in the low spin state, which for octahedral coordination has no unpaired electrons. The 3d orbital triplet is completely filled while the doublet is empty. If the Fe-S interaction is strong enough to cause a low spin configuration of the iron it probably also involves some sharing of electrons. This is also implied by the inter-nuclear distance of 2.26Å, which is much less than the sum of ionic radii, 2.60Å.

Pyrite crystallizes in the cubic system. The space lattice resembles that of NaCl with Fe$^{2+}$ replacing the Na$^+$ and S$_2^{2-}$ replacing the chloride. The inter-nuclear distance in S$_2$ is 2.18Å and the molecular axes are distributed over the four (111) orientations. The Fe atoms and the molecular centres are each on a face-centered cubic lattice of cube edge 5.42Å. Each S atom is tetrahedrally coordinated with one S neighbour (the other half of the S$_2$ molecule) and the Fe neighbours. The next nearest sulfur neighbours are six at 3.66Å. Each Fe is at the centre of an octahedron of sulphur atoms. Although all six Fe-S distances are equal, the octahedron is not perfect, but is slightly compressed along one axis. Some of the physical properties of pyrite are given in table-1.1.

Pyrite is found as both n- and p- type semiconductor with the latter distinctly higher in resistivity$^5$. 
### TABLE-1.1: Physical properties of Pyrite

<table>
<thead>
<tr>
<th>Name of the phase</th>
<th>-</th>
<th>Pyrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Name</td>
<td>-</td>
<td>Ferrous disulphide</td>
</tr>
<tr>
<td>Composition</td>
<td>-</td>
<td>FeS₂</td>
</tr>
<tr>
<td>Structure</td>
<td>-</td>
<td>Cubic</td>
</tr>
<tr>
<td>Structure type</td>
<td>-</td>
<td>Pyrite</td>
</tr>
<tr>
<td>Fe Valence</td>
<td>-</td>
<td>2⁺</td>
</tr>
<tr>
<td>Colour</td>
<td>-</td>
<td>Brass-yellow</td>
</tr>
<tr>
<td>Density</td>
<td>-</td>
<td>5.0 g cm⁻³</td>
</tr>
<tr>
<td>Mohr hardness</td>
<td>-</td>
<td>6 - 6.5</td>
</tr>
<tr>
<td>m.p</td>
<td>-</td>
<td>1171°C</td>
</tr>
<tr>
<td>Temperature of decomposition</td>
<td>-</td>
<td>687°C</td>
</tr>
<tr>
<td>Molecule per unit cell</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Cell dimension a₀</td>
<td>-</td>
<td>5.4175</td>
</tr>
<tr>
<td>Cell volume</td>
<td>-</td>
<td>159 x 10⁻²⁴ cm⁻³</td>
</tr>
<tr>
<td>Molar volume</td>
<td>-</td>
<td>23.94 cm³</td>
</tr>
<tr>
<td>X-ray density</td>
<td>-</td>
<td>5.0116 g cm⁻³</td>
</tr>
<tr>
<td>Semiconduction type</td>
<td>-</td>
<td>n, p.</td>
</tr>
</tbody>
</table>

Source - Lowson⁴
The total all India recoverable reserves of pyrites are placed at 85.481 million tonnes of which 15.464 million tonnes are under proved category, 64.695 million tonnes probable category and the remaining 5.322 million tonnes are possible category. The important deposits of pyrite are at Amjhore in Bihar and Saladipur in Sikar district of Rajasthan. The other deposits are at Kurnool of Andhra Pradesh, Chitradurga of Karnataka and North Arcot of Tamil Nadu.

THERMAL OXIDATION AND DECOMPOSITION OF PYRITE:

Most of the reactions of a process involving solid particulate reactants are heterogeneous in nature. That means reactants of such a process belong to at least two different phases. Rate controlling processes in such systems generally involve reactions at interface. Although the basic principles are same, the approach to study the kinetics of heterogeneous reactions is different from that of homogeneous reactions. A comprehensive account of the kinetics of heterogeneous reactions has been presented by Habashi. Interaction between two phases takes place through the following steps:

(a) Diffusion of reacting molecules through the interface layer.
(b) Absorption of the reactants at the surface
(c) Reaction at the interface.
(d) Desorption of the products

(e) Diffusion of the products away from the interface.

Any one of these may be rate controlling. In most of the cases, the reaction rate depends on the total surface area of the solid available for reaction. If the surface area does not change during reaction the rate can be computed easily. But when the surface area changes during the course of a reaction, it becomes difficult to compute the surface area from time to time and hence, the rate. Recently, rate equations\(^7,8\) have been developed incorporating fraction of solid reacted where the continuous changes in surface area are taken into account. For example, the expression:

\[ 1 - (1 - \alpha)^{1/3} = k t \quad \ldots \quad (1.3) \]

Describes the rate for spherical particles where \(\alpha\) is the fraction of solid reacted, 't' is the time of reaction and 'k', the rate constant. When products of reactions accumulate on a reacting surface, diffusion through these products may be rate controlling. In that case, the general equation in terms of fractions reacted \(\alpha\) is:

\[ 1 - \frac{4}{3} \alpha - (1 - \alpha)^{1/3} = k t \quad \ldots \quad (1.4) \]

Pyrite becomes very reactive at elevated temperatures. The thermal behaviour of pyrite has been studied by thermoanalytical and other techniques and in the
literature contradictory views regarding the mechanism of thermal oxidation of pyrite are expressed. Some workers suggest that the oxidation of pyrite proceeds primarily through the formation of sulphates which latter decomposes to ferric oxide and $SO_2$. Others hold that the primary products of oxidation are the oxides which subsequently reacts with sulphur dioxide to produce sulphates. It is also reported that oxidation of pyrite is accompanied by thermal decomposition to pyrrhotite ($FeS$).

According to Spektor et al. (1972), during thermal analyses, pyrite oxidation starts at $285^\circ C$ forming iron sulphate. Then two endothermic peaks appear in the DTA curve at $534-585^\circ C$ and $640-650^\circ C$ which are assigned to sulphate decomposition and pyrite dissociation respectively. Gupta et al. (1981) reported that the oxidation of pyrite proceed in the following sequence:

$$FeS_2 \rightarrow FeSO_4 \cdot 7H_2O \rightarrow \alpha - Fe_2O_3 \text{ and/or}$$

$$Fe_2(SO_4)_3 \rightarrow \alpha - Fe_2O_3$$

Banerjee (1976) performed DTA and DTG study of pyrite oxidation and decomposition and reported that pyrite was oxidised directly to iron (II) sulphate and no pyrrhotite was detected. Iron(II) sulphate was decomposed to oxide through normal and basic ferric sulphate.
formation. Banerjee and Rangaswamy investigated pyrite oxidation in fixed bed and reported that oxidation of pyrite to the extent of 98.8% was achieved at 415°C in 15 minutes. They reported also the elimination of sulphur is enhanced with increase in the silica content of the ore. Banerjee et al. (1980) studied oxidation of pyrite in dynamic air with the help of DTA, DTG, TG and XRD and reported that direct oxidation of pyrite to iron(II) sulphate favoured up to 270°C, followed by interaction of iron(II) sulphate with pyrite, direct oxidation of pyrite to ferric oxide and decomposition of iron(II) sulphate. They suggested also the presence of silica facilitates the oxidation of pyrite through adsorption of oxygen. Banerjee and Sood (1981) studied the catalytic effect of Fe$_2$O$_3$ on pyrite oxidation in air and reported that the oxidation appeared to be autocatalysed by ferric oxide. Banerjee et al. (1985) investigated pyrite oxidation in static air and postulated that the catalytic effect of silica and ferric oxide is due to the increased adsorption of oxygen. Luganov and Shabalin (1982) suggested that surface adsorbed oxygen starts reacting prior to the decomposition of pyrite and later these oxidative products interact with the sulfide grains with endothermic effect at 450-500°C and 550-570°C. Paulik et al. (1962) found that pyrite is oxidised chiefly to ferrous sulphate.
and less to ferric sulphate in air and these compounds decompose at about 700°C.

In another work, Paulik et al. (1982) suggested the pyrrhotite (FeS) route of pyrite oxidation. They reported the following reaction stoichiometries:

\[
\begin{align*}
\text{FeS}_2 & \rightarrow \text{FeS} + S \quad \ldots \quad (1.5) \\
\text{FeS} + O_2 & \rightarrow \text{Fe}_2\text{O}_3 - x (\text{SO}_4)_x \quad \ldots \quad (1.6) \\
\text{Fe}_2\text{O}_3 - x (\text{SO}_4)_x & \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_3 \quad \ldots \quad (1.7)
\end{align*}
\]

The reactions (1.5) and (1.7) are endothermic processes where reaction (1.6) is an exothermic process. Lozhkin (1973) reported a schematic coarse of pyrite oxidation which was through FeS formation also.

FeS \(\rightarrow\) FeS\(_2\) \(\rightarrow\) Fe\(_2\)S\(_3\) \(\rightarrow\) FeS \(\rightarrow\) FeSO\(_4\) \(\rightarrow\) FeO, Fe\(_2\)O\(_3\) \(\rightarrow\) Fe\(_2\)O\(_3\)

The process consists of thermal dissociation and oxidation proceeding simultaneously accompanied by diffusion. Blachere (1966) has shown that FeS formation is favoured when the atmosphere is low in oxygen, Fe\(_2\)O\(_3\) is formed under good oxidising conditions. Jorgensen and Moyle (1982) have reported that hematite is formed directly on pyrite surface below 404°C.
Pyrrhotite becomes a stable form above 552°C and in higher temperatures magnetite is formed. Ferrous and ferric sulphates are formed at temperature 583 and 644°C, respectively. Paulik et al\textsuperscript{18}, Divkovic & Milosavljevic\textsuperscript{22} and also Berg et al\textsuperscript{23} have reported three remarkable exothermic effects on the DTA curve in the course of pyrite oxidation, the first is at a temperature of 450-480°C, the second at 530-570°C and the third at 630-690°C. Divkovic and Milosavljevic\textsuperscript{22} assigns the first effect to dissociation of FeS\textsubscript{2} to FeS and S. It is supported by the fact that there is no mass change effect in TG curve at this temperature. The 2nd peak is assigned to sulphur oxidation to sulphur dioxide. There is a weight loss effect in the TG curve at this point. The third exothermic peak corresponds to sulfate formation. There is an increase of weight effect in the TG curve at this temperature. They have reported the reaction stoichiometries as follows:

\begin{align*}
2\text{FeS}_2 &\rightarrow 2\text{FeS} + \text{S}_2 & \ldots & (1.5) \\
\text{S}_2 + 2\text{O}_2 &\rightarrow 2\text{SO}_2 & \ldots & (1.8) \\
\text{FeS} + 2\text{O}_2 &\rightarrow \text{FeSO}_4 & \ldots & (1.9)
\end{align*}

The reaction rates and kinetics of pyrite oxidation also have been studied by many authors. Samal\textsuperscript{24} (1965) has reported that the decomposition process
is satisfactorily described by the kinetic equation
\(1 - (1 - \alpha)^{\frac{1}{3}} = kt\) at a temperature range of 486-578°C
and the equation is valid for \(\alpha = 60-70\%\) in his experimental conditions. Mendelsohn et al\(^{25}\) (1959) have
done the kinetic study of pyrite roasting performing experiments in a horizontal electric heated furnace
and monitoring the exit \(\text{SO}_2\) gas. The reaction is 1st order in the initial period. After an initial period
the rate decreases owing to an increase of the resistance to the diffusion of \(\text{O}_2\) into the interior of the granules.
The low value of activation energy, i.e., 6.508 K cal/mole shows that diffusion of oxygen is the rate determining
factor for the entire process. Pataridze\(^{26}\) (1985) reported that oxidation of pyrite starts at temperature
about 430°C and a product hematite crust is formed on the pyrite eventually which prevented further oxidation.
Prasad et al\(^{27}\) (1985) studied the kinetics of roasting of pyrite by Mössbauer spectra and XRD and
reported the optimum reaction conditions for efficient transformation of pyrite into \(\alpha - \text{Fe}_2\text{O}_3\) and \(\gamma - \text{Fe}_2\text{O}_3\).
According to Luganov and Shabalin\(^{16}\) (1982) pyrite oxidation process is diffusional type at low temperatures
and becomes chemical type as temperature rises.

**AQUEOUS OXIDATION OF PYRITE:**

Aqueous oxidation of pyrite has drawn scientific interest for more than 100 years\(^3,28,29\). As pyrite
oxidation in nature is the cause of a serious environmental problem, extensive work has been done to study the mechanism of the oxidation in order to find a solution for the problem and to utilise this oxidation process for economical extraction of some valuable metals. Lowson\textsuperscript{4} has discussed the chemistry of the aqueous oxidation of pyrite during commercial application and consequent environmental hazard. There are three possible pathways for the aqueous oxidation of pyrite. These are:

(i) Through bacterial catalysts,
(ii) Through a sequence of chemical reactions\textsuperscript{5} and
(iii) Through an electrochemical reaction.

Bacterial oxidation is not in the purview of this work. In experiments below 100°C for the study of pyrite oxidation through the other two paths, care must be exercised to exclude bacterial activity. Two oxidants viz., molecular oxygen and ferric ion have been taken by different investigators for the study of chemical oxidation of pyrite.

By Molecular Oxygen:

There are two oxidizable species in pyrite, the ferrous iron and sulphidic sulphur. Nelson et al\textsuperscript{30} postulated that during the oxidation of pyrite only
the sulphidic sulphur is oxidised and iron passes into solution in the ferrous state (eqn. 1.10).

\[ 2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \]  

(1.10)

The ferrous iron may be oxidised in the subsequent step. There are at least two side reactions. One forms elemental sulphur and the other forms thiosulphate and sulphite intermediates. Steger and Desjardins\(^{31}\) considered thiocompounds as a minor product. McKay and Halpern\(^ {32} \) (1958) proposed the following reaction sequence for the oxidation of pyrite in nature:

\[ 2\text{O}_2 + \text{FeS}_2 \rightarrow \text{FeS}_2(2\text{O}_2)_{\text{ads}} \rightarrow \text{Fe}^{2+}_{\text{aq}} + \text{SO}^{2-}_{4\text{aq}} + \text{S}^0 \]  

(1.11)

They also reported that this reaction fails to account for the observed production of \( \text{Fe}^{3+} \). They observed both \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) ions as well as elemental sulphur in varying amounts during the aqueous oxidation of pyrite. In the absence of any \( \text{H}_2\text{SO}_4 \) all the sulphur in pyrite is converted to sulphate and no elemental sulphur is formed. When the solution contains 0.15M \( \text{H}_2\text{SO}_4 \) initially no additional free acid is formed and the sulphaide is oxidised to elemental sulphur and ferrous to ferric sulphate.

According to Habashi\(^ {33} \) (1969) aqueous oxidation of pyrite follows two different paths depending on the
pH of the medium. At very low pH the formation of elemental sulphur is favourable and with increasing pH the formation of sulphate is favourable. The following reaction take place at extreme cases:

\[
\begin{align*}
    \text{FeS}_2 + 2\text{H}^+ + \frac{1}{2}\text{O}_2 & \rightarrow \text{Fe}^{++} + \text{H}_2\text{O} + 2\text{S} \quad \ldots \quad (1.12) \\
    \text{FeS}_2 + \text{H}_2\text{O} + 7/2 \text{O}_2 & \rightarrow \text{Fe}^{++} + 2\text{H}^+ + 2\text{SO}_4^{--} \quad \ldots \quad (1.10)
\end{align*}
\]

Singer and Stumm\textsuperscript{34,35} and Stumm and Morgan\textsuperscript{36} (1970) proposed the following sequence of chemical steps for the reaction path in the context of acid mine drainage:

\[
\begin{align*}
\text{FeS}_2 + \text{O}_2 & \rightarrow \text{SO}_4^{--} + \text{Fe}^{3+} + \text{S}_2 \quad \text{Fast} \\
\text{FeS}_2 + \text{O}_2 & \rightarrow \text{SO}_4^{--} + \text{Fe}^{3+} \quad \text{Slow}
\end{align*}
\]

Each of these reactions may be observed individually and may occur in an environmental situation independently of the overall reaction. Mizoguchi and Habashi\textsuperscript{37} (1983) reported that pyrite oxidation is faster in mild H\textsubscript{2}SO\textsubscript{4} than in mild HCl. They also reported that a mixture of pyrite and ZnS increases the rate of oxidation of
ZnS due to a galvanic action in which pyrite acts as cathode and ZnS as anode.

**Aqueous Oxidation of Pyrite by Ferric Ion:**

The use of ferric ion as an oxidant for pyrite has been widely reported. The general aspects of ferric ion leaching have been discussed by Dutrizac and MacDonald\(^{38}\) (1974). It has been pointed out from the Eh-pH diagrams that base metal sulphides require the presence of an oxidising agent to affect their dissolution. Peters\(^{39}\) has put forward the following equation for the oxidising potential of the Fe\(^{3+}/\)Fe\(^{2+}\) couple at 25°C.

\[
E = 0.771 + 0.059 \log \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}} \quad \ldots \quad (1.13)
\]

This equation indicates that solution containing even traces of Fe\(^{3+}\) in comparison to Fe\(^{2+}\) have an oxidising potential higher enough to affect the dissolution of pyrite. Garrels and Thompson\(^{40}\) (1960) investigated pyrite oxidation in Fe(III) sulphate solution by monitoring the redox potential and postulated the overall reaction as equation (1.14).

\[
\text{FeS}_2 + 8\text{H}_2\text{O} + 14\text{Fe}^{3+} \longrightarrow 2\text{SO}_4^{2-} + 15\text{Fe}^{2+} + 16\text{H}^+ \quad \ldots \quad (1.14)
\]
Thomas and Whalley\textsuperscript{41} studied the oxidation of pyrite at 90°C with ferric sulphate solutions and proposed the stoichiometry as:

\[
\text{FeS}_2 + 7\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O} \rightarrow 15\text{FeSO}_4 + 8\text{H}_2\text{SO}_4 \ldots \quad (1.15)
\]

which is similar to 1.14. More recently, the commercial use of ferric ion has been considered for the desulphurisation of coal. Sulphur is present dominantly as pyrite in coal and an ideal clearing process could be to remove this sulphur as soluble sulphate without oxidising the coal. Mathews and Robins\textsuperscript{42} studied the reaction over a pH range of 0 to 1.5 with initial Fe$^{3+}$ concentrations of about 0.01M and over a temperature range of 30-70°C. In addition, the effects of slurry density $D$, surface area $S$, carrier anions, and Cu$^{2+}$ ion was studied. They reported the overall stoichiometry as equation (1.14) and final rate expression was expressed as equation (1.16).

\[
-\frac{d[\text{Fe}^{3+}]}{dt} = k \frac{DS[\text{Fe}^{3+}]}{[\text{Fe}][\text{H}]^{0.44}} \ldots \quad (1.16)
\]

where \( k = 2.29 \times 10^{-9} \text{ M}^{0.56} \text{ S}^{-1} \) and the activation energy was 85 kJ M$^{-1}$. However, there was no evidence for sulphur forming reaction. This contrasted the results of Tseft and Tatarinova\textsuperscript{43} (1958) who investigated the pressure leaching of pyrite at 220-240°C with a
number of oxidants including ferric chloride and ferric sulphate. They reported that pyrite is not readily soluble perhaps due to the formation of a passivating elemental sulphur film. Ferric chloride was found to be more effective leaching agent under their experimental conditions. Rath et al. investigated pyrite oxidation in ferric chloride solution and reported that reaction (1.14) and (1.17) proceed simultaneously at a ratio of 2:1.

\[
\text{FeS}_2 + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+} + 2\text{S}^0 \quad \text{... (1.17)}
\]

Zheng et al. (1986) investigated the oxidation of pyrite in ferric sulphate solution and reported the overall reaction (1.14) to be valid. The oxidation rate depends on the total iron concentration and on the ratio of ferric to ferrous ions under constant acid concentration. Woodcock observed that ferric ion is more oxidising agent than oxygen. But Mckay and Halperns studied the oxidation of pyrite at 110°C by ferric ion in 0.075M H$_2$SO$_4$ and reported that ferric ion is a poor oxidizer compared to molecular oxygen.

ELECTROCHEMICAL OXIDATION OF PYRITE :

Pyrite shows a rest potential of +0.63V vs. SHE in 1M H$_2$SO$_4$. Bailey and Peters (1976) postulated
that the pyrite reacts with water at an anodic site as per equation (1.18)

\[
FeS_2 + 8H_2O \rightarrow Fe^{3+} + 2SO_4^{2-} + 16H^+ + 15e^- \quad ... \quad (1.18)
\]

At cathodic site oxygen is reduced to water.

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \quad \quad ... \quad (1.19)
\]

If the acid strength is increased beyond 0.17M \(H_2SO_4\) the leaching reaction becomes an acid consumer rather than acid generator. Andriamanana and Lamache\(^{49}\) (1983) studied the electrochemical behaviour of pyrite in 1M \(H_2SO_4\). The anodic oxidation of \(FeS_2\) occurs at +0.98 V Vs SCE and leads to the formation of \(Fe^{3+}\), \(S\) and \(H_2SO_4\). The reduction of \(FeS_2\) to \(Fe^{2+}\) and \(H_2S\) occurs at -0.50 V Vs SCE. Peters and Majima\(^{50}\) investigated the electrochemical reaction of pyrite in acid perchlorate solutions. The results of their experiments indicated that pyrite could be cathodically dissolved below a potential of 0.62V Vs SHE. The reaction products were \(Fe^{2+}\) & \(H_2S\).

\[
FeS_2 + 4H^+ + 2e^- \rightarrow Fe^{2+} + 2H_2S \quad \quad \quad ... \quad (1.20)
\]

The current efficiency for reaction (1.20) was found to be very low, generally less than 35%. Hydrogen formation was the main reaction. The oxidation of
pyrite was found to occur above 0.62 V Vs. SHE, the products being Fe$^{3+}$ and SO$_4^{2-}$. Based on reaction (1.18), the current efficiency was nearly 100%. No elemental sulphur was detected. Biegler and Swift$^{51}$ performed coulometric experiments for pyrite dissolution in 1M H$_2$SO$_4$, 1M HClO$_4$ and 1M HCl. They reported that anodic dissolution of FeS$_2$ produces both SO$_4^{2-}$ (reaction 1.18) and elemental sulphur (reaction 1.21):

$$\text{FeS}_2 \rightarrow \text{Fe}^{3+} + 2\text{S}^0 + 3e^- \quad \cdots \quad (1.21)$$

The coulometric results were interpreted in terms of a combination of reactions (1.18) and (1.21). The overall process they reported as equation (1.22).

$$\text{FeS}_2 + 8x\text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2x\text{SO}_4^{2-} + 2(1-x)\text{S} + 16x\text{H}^+ + (12x + 3)e \quad (1.22)$$

'x' is the fraction of pyrite reacting as per equation (1.18) (equivalent to the % yield of sulphate). Kametani and Aoki$^{52}$ conducted experiments on oxidation leaching of chalcopyrite concentrate containing pyrite in mild sulphuric acid at 90°C. The potential of suspension was maintained by controlled oxidation of Fe$^{3+}$/Fe$^{2+}$ couple of the solution with KMnO$_4$. They reported that the oxidation of pyrite takes place only above 0.45 V. Vs. SCE and yields sulphate ion.
STRUCTURAL CHARACTERISTICS OF MANGANESE OXIDES:

Manganese forms a series of oxides containing the oxidation states of +2, +3, +4, and +7. Out of these, manganese (IV) oxides have got tremendous importance which is used as a cathode material and also a catalyst. Most of these oxides exhibit considerable deviation from stoichiometry and this characteristic has evoked interest in the recent past among solid state physicists and chemists.

Manganese (IV) oxides occur freely in nature and more than 20 oxide phases are recognised as valid mineral species. Many of these minerals have been synthesized and studied for electrochemical and other applications. Burns and Burns after a detailed investigation have assembled all published data and classified the dioxide minerals. The following major modifications of dioxide are known: $\alpha$-MnO$_2$, $\beta$-MnO$_2$, $\gamma$-MnO$_2$ and $\delta$-MnO$_2$. Each of them represent a number of minerals. The various forms have often been described as polymorphs of MnO$_2$. Manganese dioxide cannot be classified solely on the basis of chemical composition. The X-ray diffraction technique serves to distinguish between the different phases and in some instances to locate the position of the ions within the unit cell. Minor structural
differences may affect the behaviour of the sample significantly. Besides, different products may be produced by small variations in the method of preparation and subsequent treatment. One encounters in the literature on MnO₂ not only mineral names like pyrolusite, psilomelane, cryptomelane, ramsdellite, hollandite, coronadite, etc., but the Greek designations like \( \alpha, \beta, \gamma, \delta, \zeta, \kappa \) and \( \rho \) and also subspecies like \( \alpha', \alpha'', \gamma', \gamma'' \), etc. There are a few types of products which occur more frequently or significantly among the many varieties encountered and which are susceptible to distinct characterisation with respect to;

(1) Their structure (as revealed by X-ray and electron diffraction)

(2) Their morphology (as observed by electron diffraction)

(3) Their composition (as revealed by wet chemical, spectroscope methods)

(4) Their genetic history (in terms of relevant chemical and physical environments during the formation and any subsequent treatment).

From the above criteria of classifying MnO₂, it is now almost universally accepted that there exists five distinct phases of MnO₂. There are: well crystallised battery inactive \( \alpha' \)-MnO₂ and its isostructural minerals like cryptomelane, hollandite, psilomelane,
coronadite, etc., \( \beta \)-MnO\(_2\) and its isostructural mineral pyrolusite; the mesocrystalline \( \gamma \) and \( \rho \)-MnO\(_2\) and its iso-structural mineral like nsutite; semiamorphous embryonic stystallite of the type \( \delta \)-MnO\(_2\) and its iso-structural mineral like birnessite; and highly crystalline orthorhombic MnO\(_2\) known as ramsdellite. It has been frequently observed that the above modifications of MnO\(_2\) rarely exist as single phase in either synthetic or natural MnO\(_2\) samples. Existence of two or more phases is more of a rule rather than an exception. Nye et al.\(^{54}\) discussed the structural characteristics of all individual manganese dioxides. Some of the important structural characteristics\(^ {55}\) of different polymorphic forms of MnO\(_2\) are given in Table-1.2.

GENERAL CHARACTERISTICS OF MANGANESE ORES:

More than 300 different minerals contain manganese of which perhaps a dozen are important. The oxides constitute the most important manganese ore minerals. Pyrolusite, a manganese dioxide is the most common manganese oxide mineral. Other important oxides include manganite (Mn\(_2\)O\(_3\), H\(_2\)O) a manganese oxide hydrate; cryptomelane, a potash bearing oxide of variable composition and hausmanite (Mn\(_3\)O\(_4\)). Psilomelane is the name given to a hydrate-barium manganese oxide mineral and also applied to hard unidentified manganese oxides.
Table 1.2 Structural properties of different polymorphic forms of manganese dioxide

<table>
<thead>
<tr>
<th>Polymorphic MnO₂</th>
<th>Natural occurring minerals</th>
<th>Crystal system</th>
<th>Empirical formula</th>
<th>Mn%</th>
<th>Unit cell dimensions (Å)</th>
<th>Cell volume (Å³)</th>
<th>No. of formula units/(z)*</th>
<th>Specific gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.9 -MnO₂</td>
<td>Crypto-melane Hollandite type</td>
<td>Tetragonal</td>
<td>MnO₁.₉₂(OH)₀.₀₄(NH₄)₀.₀₂</td>
<td>58.86</td>
<td>a: 9.95, b: 9.95, c: 2.90</td>
<td>286.97</td>
<td>7.53</td>
<td>3.80</td>
</tr>
<tr>
<td>8.8 -MnO₂</td>
<td>Pyrolusite (Rutile type)</td>
<td>Tetragonal</td>
<td>MnO₁.₉₂(OH)₀.₀₄(0.17H₂O)</td>
<td>62.95</td>
<td>a: 4.43, b: 4.43, c: 2.88</td>
<td>56.43</td>
<td>1.93</td>
<td>4.90</td>
</tr>
<tr>
<td>9.9 -MnO₂</td>
<td>Nsutite Orthorhombic</td>
<td></td>
<td>MnO₁.₉₄(OH)₀.₀₇(0.22H₂O)</td>
<td>60.33</td>
<td>a: 4.43, b: 10.75, c: 2.71</td>
<td>128.95</td>
<td>4.20</td>
<td>4.70</td>
</tr>
<tr>
<td>α-MnO₂</td>
<td>Birmesite Hexagonal</td>
<td></td>
<td>MnO₁.₈₄(OH)₀.₁₆K₀.₀₈(0.34H₂O)</td>
<td>56.83</td>
<td>a: 7.77, b: 7.77, c: 11.08</td>
<td>579.08</td>
<td>12.30</td>
<td>3.18</td>
</tr>
</tbody>
</table>

(z)* = Unit cell

Data from the investigation of Paridà.⁵⁵
Wad refers to soft, unidentified mixtures. The principal manganese carbonate ore is rhodochrosite (MnCO₃). Rhodonite (MnSiO₃) and braunite (3Mn₂O₃, MnSiO₃) are two silicate manganese ore minerals. Table 1.3 shows the composition and physical properties of some frequently occurring manganese minerals.

Though manganese is relatively an abundant element in earth's crust, the economic reserves are concentrated in limited geographical areas. The world reserves of manganese ore is estimated at around 1,200 crores short tonnes. Out of this 850 crore short tonnes are in the Republic of South Africa and 250 crore short tonnes are in USSR. Other major deposits are in Brazil, West Africa, India and Australia. India holds seventh position in the world in manganese ore reserves. In India the reserve estimate of manganese ore is around 135 million tonnes. Out of this, only about 18% is in the grades of 46% and above Mn; about 26% is in the grade of 35 to 46% Mn and balance belongs to inferior grades or unclassified. This major portion of low grade ores has no use unless technology development and proper planning for judicious use of all the available resources are done.

Pyrolusite is a relatively good conductor for an oxide mineral. Resistivity value as low as $1 \times 10^{-3}$
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Colour</th>
<th>Mn(%)</th>
<th>Hardness</th>
<th>Specific gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolusite</td>
<td>MnO₂</td>
<td>Steel grey to black</td>
<td>63.2</td>
<td>6-7</td>
<td>5</td>
</tr>
<tr>
<td>Ramsdellite</td>
<td>MnO₂</td>
<td>Dark grey to black</td>
<td>63</td>
<td>3</td>
<td>4.7</td>
</tr>
<tr>
<td>Polianite</td>
<td>MnO₂</td>
<td>Black to steel grey</td>
<td></td>
<td>6-6.5</td>
<td>5</td>
</tr>
<tr>
<td>Manganite</td>
<td>Mn₂O₃·H₂O</td>
<td>Black to steel grey</td>
<td>62</td>
<td>4</td>
<td>4.3</td>
</tr>
<tr>
<td>Cryptomelane</td>
<td>K₂Mn₈O₁₆</td>
<td>Black to steel grey</td>
<td>45-60</td>
<td>5-6</td>
<td>4.3</td>
</tr>
<tr>
<td>Psilomelane</td>
<td>BaMn₉O₁₈·2H₂O</td>
<td>Black to dark grey</td>
<td>5-6</td>
<td></td>
<td>4.4-4.7</td>
</tr>
<tr>
<td>Hausmanite</td>
<td>MnMn₂O₄</td>
<td>Brown to black</td>
<td>72</td>
<td>4.8</td>
<td>4.7-5.0</td>
</tr>
<tr>
<td>Braunite</td>
<td>3Mn₂O₃·MnSiO₃</td>
<td>Brown to black</td>
<td>50-60</td>
<td>6.0-6.5</td>
<td>4.7-4.9</td>
</tr>
<tr>
<td>Bixbyte</td>
<td>(Mn,Fe)₂O₃</td>
<td>Black</td>
<td>30-40</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Jacobsite</td>
<td>MnFe₂O₄</td>
<td>Black</td>
<td>24</td>
<td>6</td>
<td>4.8</td>
</tr>
<tr>
<td>Hollandite</td>
<td>BaMn₈O₁₆</td>
<td>Black to steel grey</td>
<td>6</td>
<td>4.5-5.0</td>
<td></td>
</tr>
<tr>
<td>Coronadite</td>
<td>PbMn₈O₁₆</td>
<td>Black to steel grey</td>
<td></td>
<td>5.2-5.6</td>
<td>4.5-5.0</td>
</tr>
<tr>
<td>Rhodochrosite</td>
<td>MnCO₃</td>
<td>Red-rose to brown</td>
<td>48</td>
<td>3.5-4.5</td>
<td>3.3-3.6</td>
</tr>
<tr>
<td>Rhodonite</td>
<td>MnSiO₃</td>
<td>Pink</td>
<td>42</td>
<td>5.5-6.5</td>
<td>3.4-3.6</td>
</tr>
<tr>
<td>Alabandite</td>
<td>MnS</td>
<td>Iron-black</td>
<td></td>
<td>3.5-4</td>
<td>3.95</td>
</tr>
<tr>
<td>Wad</td>
<td>Variable</td>
<td>Dull black to brown-black</td>
<td></td>
<td>5-6</td>
<td>3-4.28</td>
</tr>
</tbody>
</table>

Source: Weiss
Ohm-m for pyrolusite has been reported\textsuperscript{59}. But the values measured by different investigators varies widely because of all measurements have been on porous microcrystalline materials with a density rather less than the theoretical 5.23 gm. cm\textsuperscript{-3}. The resistivity is strongly correlated with density. Klose\textsuperscript{60} carried out measurements on synthetic pyrolusite of varying densities. For samples having densities of 2.5, 4.0 and 4.7 gm cm\textsuperscript{-3}, he reported the resistivities as $10^{-1}$, $10^{-5}$ and $3 \times 10^{-3}$ Ohm-m, respectively. Baking in air at temperature up to 300°C lower the resistivity by up to two orders of magnitude\textsuperscript{61} probably due to removal of chemisorbed water. Pyrolusite is an n-type conductor.

**COMMERCIAL IMPORTANCE OF MnSO\textsubscript{4}**: 

Manganese (II) sulphate is one of the most stable manganese (II) compound known. It is probably the most important manganous salt in commerce, being the starting point in the manufacture of most other manganese compounds. Manganese sulphate has a wide range of direct end uses and is an intermediary in the production of most manganese compounds. It is a stepping stone in the production of synthetic MnO\textsubscript{2}, electrolytic manganese metal and in hydrometallurgical and chemical processes employing manganese.
Manganese sulphate is an excellent source of readily available manganese for plant life because in sulfate form, the manganese dissolves quickly after application and is immediately available to the plant. Manganese sulphate mixed in mineral feeds is an economical source of nutritionally available manganese. It is one of the several salts used as a dietary supplement to incorporate manganese into the human diet also. Since the early 1930s most MnSO₄ used in agriculture as a nutrient and later fungicide has been a by-product resulting from the manufacture of hydroquinone. The world production of MnSO₄ by this indirect way is about 85,000 tons per year (tpy). Direct production of manganese sulphate world-wide for re-sale is approximately 55,000 tpy. The world-wide production of merchant manganese sulphate is thus estimated at 140,000 tpy to which should be added an additional 50,000 tpy produced as in-house production as a step in the manufacture of fungicides.

SULPHATIZATION ROASTING OF MANGANESEDIOXIDES:

A number of combination of sulphatizing and reducing agents have been used by different investigators for the sulphatizing roasting of manganese dioxides. These include iron (II) sulphate, SO₂, SO₃, C, H₂SO₄.
and (NH$_4$)$_2$SO$_4$. MnSO$_4$ is commercially obtained by the action of H$_2$SO$_4$ and a reducing agent on MnO$_2$.

$$2\text{MnO}_2 + \text{C(coal)} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{MnSO}_4\cdot\text{H}_2\text{O} + \text{CO}_2 \quad \ldots \quad (1.23)$$

It is also manufactured by roasting of a mixture of pyrolusite (MnO$_2$), ferrous sulfate and coal followed by leaching and crystallization.

The formation of a number of phases during the sulphatization roasting of manganese dioxide have been reported which include different manganese oxide phases, manganese sulphate and thiosulphates. The areas of stability for MnSO$_4$, MnO$_2$, Mn$_2$O$_3$, and Mn$_3$O$_4$ in the Mn-S-O system are shown in predominance area diagram, log P$_{O_2}$ versus log P$_{SO_2}$ (Fig. 1.1). The diagram is drawn for two temperatures viz., 700°K and 1100°K. From the fact that the boundary layer between the area of stability of MnO$_2$ and MnSO$_4$ at 700°K is parallel to the obscissa, it is evident that MnO$_2$ converts to MnSO$_4$ irrespective of oxygen pressure and the conversion depends only upon the SO$_2$ pressure in the system. The decomposition temperature for different metal sulphates play an important role for the selective sulphatization of manganese in low grade manganese.
Fig. 1.1: Predominance area diagram for the Mn-S-O system at 700°K and 1100°K (diagram from Igraham and Mariers, 1968).
ores. Apart from manganese, low grade ores contain metals like iron, aluminium, calcium, magnesium, potassium, sodium, etc., as major or minor constituents. The decomposition temperature of some metal sulphates which are relevant to the present work are given in Table 1.4.

Manganese oxides are effective absorbents for SO₂ and SO₃. Ingrahm and Marier (1968) examined the kinetics of the sulfation of MnO₂, Mn₂O₃, and Mn₃O₄ in SO₂, SO₃ and O₂ mixtures with the help of a thermogravimetric balance. The descending order of sulfation rates at temperatures near 400°C was found to be Mn₂O₃ > MnO₂ > Mn₃O₄. The following reactions have been reported with respective activation energy values:

\[
\begin{align*}
\text{MnO}_2 + \text{SO}_2 & \rightarrow \text{MnSO}_4 & \quad \text{12 Kcal/mole} \quad (1.24) \\
2\text{Mn}_2\text{O}_3 + 4\text{SO}_2 + \text{O}_2 & \rightarrow 4\text{MnSO}_4 & \quad \text{19 Kcal/mole} \quad (1.25) \\
\text{Mn}_3\text{O}_4 + 3\text{SO}_2 + \text{O}_2 & \rightarrow 3\text{MnSO}_4 & \quad \text{21 Kcal/mole} \quad (1.26)
\end{align*}
\]

The thermal decomposition of MnO₂, Mn₂O₃ and MnSO₄ also have been examined and following stoichiometries have been reported:

\[
\begin{align*}
4\text{MnO}_2 & \rightarrow 2\text{Mn}_2\text{O}_3 + \text{O}_2 & \quad \text{39 Kcal/mole} \quad (1.27) \\
6\text{Mn}_2\text{O}_3 & \rightarrow 4\text{Mn}_3\text{O}_4 + \text{O}_2 & \quad \text{47 Kcal/mole} \quad (1.28)
\end{align*}
\]
### Table - 1.4 Decomposition temperatures of some anhydrous metallic sulphates

<table>
<thead>
<tr>
<th>Metallic sulphates</th>
<th>Temperature at beginning of decomposition °C</th>
<th>Temperature of energetic decomposition °C</th>
<th>Products of decomposition</th>
<th>Colour of products</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSO₄</td>
<td>167</td>
<td>480</td>
<td>Fe₂O₃,2SO₄</td>
<td>Yellow, brown</td>
</tr>
<tr>
<td>Fe₂O₃,2SO₄</td>
<td>492</td>
<td>560</td>
<td>Fe₂O₃</td>
<td>Red</td>
</tr>
<tr>
<td>Al₂(SO₄)₃</td>
<td>590</td>
<td>639</td>
<td>Al₂O₃</td>
<td>White</td>
</tr>
<tr>
<td>MnSO₄</td>
<td>699</td>
<td>790</td>
<td>Mn₃O₄</td>
<td>Dark red to black</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>890</td>
<td>972</td>
<td>MgO</td>
<td>White</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>1200</td>
<td>-</td>
<td>CaO</td>
<td>White</td>
</tr>
</tbody>
</table>

Source: Hodgman
Vanhecke and Bartlett (1973) also postulated reactions (1.24) and (1.25) for sulphotization of manganese dioxide with sulphur dioxide in the presence of air at elevated temperature. Murthy et al. (1987) studied the sulphotization of manganese nodule in a vertical bed reactor using SO₂ - air mixture. They reported that the highly exothermic sulphotisation reaction requires the control of reaction temperature. Itou et al. (1972) studied the reaction between SO₂ and different synthetic and natured MnO₂ samples with the aid of a thermal balance and reported that the poorly crystalline α -MnO₂ is more reactive than natural MnO₂. The rate (γ) of the reaction (1.24) was given by:

\[
\gamma = K \frac{M^0_{\text{MnO}_2}(1-x)}{P_{\text{SO}_2}} \quad \text{... (1.31)}
\]

Where 
\( M^0_{\text{MnO}_2} \) is initial amount of MnO₂
\( P_{\text{SO}_2} \) is partial pressure of SO₂
\( x \) is initial fraction of MnO₂
and, \( K \) is the rate constant.

The activation energy obtained for this reaction was 1.2-2.5 Kcal/mole. Sahoo et al. (1984) studied the
sulfation of MnO$_2$ in a SO$_2$-O$_2$ atmosphere by means of a gravimetric technique. They reported that after an initial period, the reaction rate confirmed to a parabolic growth rate indicating that the reaction was a diffusion controlled process with the formation of compact product layer. The activation energy was found to be 20 Kcal/mole. Joyce and Prasky$^{72}$ (1973) studied the sulfation of manganiferous iron ore with sulphur oxide gases for selective leaching of manganese. At one step manganese mineral was converted to water soluble manganese sulphate at 700°C. At another step, the hematite was reduced to magnetite by natural gas in the temperature range of 350-425°C. Water leaching of roasted products recovered over 90% of the manganese and magnetite concentrate was obtained from the water insoluble residue by magnetic separation. Sahoo et al.$^{73}$ (1978) have performed DTA study of sulphatization of MnO$_2$ with (NH$_4$)$_2$SO$_4$ and obtained free energy values for possible reactions. There was no correlation between the theoretical value of ΔH$^\circ$ and that calculated from DTA peak which they attributed to the uncertainty in the thermodynamic values and the possibility of some side reactions. Sahoo and Rao$^{74}$ investigated the sulphatization of low grade manganese ore with (NH$_4$)$_2$SO$_4$ and optimised the experimental variables such as amount of sulphatising agents, time and temperature with the factorial design method.
Sulphur dioxide is usually manufactured from iron pyrites by roasting at high temperatures. Manganese dioxide is one of the catalysts used for the oxidation of sulphides to sulphur dioxide. This observation is applied to study the sulfatization of manganese oxide with pyrite. Sulphatization roasting of manganese oxide with pyrite deals with interaction between two solids. A number of reactions between solids are of considerable importance in pyrometallurgical processes. Some of these reactions are true solid-solid reactions, but the interaction between manganese oxide and pyrite cannot be assumed to be solid-solid reaction. Rather, the reaction between these two occur through gaseous intermediates and these reactions may be considered better as sets of gas-solid reactions. The kinetics of these reactions thus can be computed in the light of the mathematical analyses developed for gas-solid reactions. The reaction model of a specific gas-solid reaction which is the rate controlling step can be made applicable to the overall solid-solid reaction. Even though, reduction roasting of manganese ore with pyrite have been reported earlier information on reaction mechanism and kinetic studies is not available in the literature. Most of these studies are early Russian work directed towards process development studies.
As early as 1951, Fassina and Fassina studied the roasting of pyrite with oxide of manganese in order to obtain sulphuric anhydride, \( \text{SO}_3 \). After heating at 700°C in presence of air, they got the additional products \( \text{MnSO}_4 \) and \( \text{Fe}_2\text{O}_3 \). Diev et al. (1954) were able to convert 90 to 98% of \( \text{MnO}_2 \) to \( \text{MnSO}_4 \) by heating with pyrite at a temperature of 700°C. They reported that a oxide film was formed and after an initial period, the reaction became slow. Moorthy and Datar (1951) reported a method for producing \( \text{MnSO}_4 \) from coal pyrite and \( \text{MnO}_2 \) by heating the intimate mixture at a temperature range of 300 to 350°C in presence of air. The conversion they got after 6 hours was 47 to 48%. The product was free from \( \text{S}^- \), \( \text{SO}_3^- \), \( \text{S}_2\text{O}_3^- \), and iron. Haul and Schumman (1955) studied the reaction between manganese dioxide and iron pyrites in a nitrogen atmosphere. After 20 hours heating at a temperature of 400°C and also at 950°C no \( \text{MnSO}_4 \) was formed. At these temperatures, the products were \( \text{SO}_2 \), \( \text{Fe}_3\text{O}_4 \) (Fe, Mn), \( \text{Fe}_3\text{O}_4' \), \( \text{MnS} \) and \( \text{MnO} \). They predicted a solid state reaction at 400°C and a gas-solid type reaction over 550°C. Brosch and Duarte (1976) reported a process for preparation of \( \text{MnSO}_4 \) by heating a mixture of pyrolusite, coal and pyrite at 600°C in a stream of air. They postulated that \( \text{MnO}_2 \) is first reduced to \( \text{MnO} \) by carbon monoxide.
Then MnO is converted to MnSO₃ reacting with SO₂ which is obtained after pyrite decomposition. MnSO₃ is converted to MnSO₄ by atmospheric air oxidation. Rao (1985) studied the formation of manganese sulphate in the solid state reaction of iron pyrite with synthetic and natural manganese dioxide samples. Manganese sulfate formation with synthetic manganese dioxide samples was better in comparison to natural ones. Sulfatization of low grade manganese ore with low grade pyrite has been reported by the author. It is observed that formation of manganese sulphate increases with increase in temperature in the temperature range of 200-600°C. Beyond 600°C the formation decreases due to decomposition. Silica contents of pyrite samples are beneficiary for manganese sulphate formation. The sulfatization increases with decrease in particle size and packing density of manganese ore and hence, it is suggested the reaction to be diffusion controlled. Simultaneous DTA and TGA study of sulfatization of different polymorphs of MnO₂ with iron pyrites has also been reported by the author.

**REDUCTION LEACHING OF MANGANESE DIOXIDE:**

Leaching, i.e., chemical extraction of metal value into aqueous phase is most important as it can be made preferential or complete by proper control
of parameters in the system. The important parameters to control the behaviour of metal ions in aqueous solution are the pH and the oxidation potential of the solution. These aspects of the thermodynamics of solutions have been discussed in detail by Burkin (1966). The pH of the solution is the main parameter controlling the solubility of oxidised or hydrolysed metal species. The oxidation potential in an aqueous solution primarily determines the valencies of oxidation states of metal and ligand species and this in turn, governs whether or not the species are soluble. The extent of oxidation required to take a metal in to solution can be known from its potential - pH (Eh-pH) diagrams. The type of anion accompanying the metal ions in solution is also an important leaching parameters as it affects the course of the process. Traditionally the leaching medium in many hydrometallurgical processes are so chosen that the anion associated with the metal ion in solution is the sulphate ion. Hydrometallurgical production of uranium, zinc and nickel are based on H₂SO₄ leaching.

Many leaching reactions are electrochemical in nature. If a semi-conducting mineral is immersed in an aqueous medium, it will assume an electrical
potential with respect to that medium. If a single mineral is involved, then both cathodic and anodic half reactions will proceed in respective areas of domains on the mineral surface and a current will flow between these domains. The anodic ($I_a$) and cathodic ($I_c$) partial currents will be equal and the net current flow ($I_g$) on the mineral surface is zero. In the actual system, the cathodic and anodic zones cannot be separated because they are short circuited. Due to continuous flow of electrons from an anodic area to a cathodic area, the system has an unique electrode potential $E$ which is less than the equilibrium potential of the cathode, $E_c$, but greater than the equilibrium potential of the anode $E_a$. $E$ is known as the compromise potential. However, as soon as an external potential is applied, the electrode potentials change owing to the creation of over-voltage. At equilibrium, the mineral adopts a mixed potential $E_{mix}$ and the galvanic current density is $I$.

When two minerals assuming different potentials in an aqueous medium are immersed in the medium, an electrochemical cell will form. The mineral with the higher rest potential will act as a cathode while the anode will be the mineral with the lower rest potential.
Sulfide minerals are semi-conductors and they assume different potentials in an aqueous medium. Pyrite shows a rest potential of +0.63 V Vs. SHE in a medium of 1M H₂SO₄. On the other hand, manganese dioxide (pyrolusite) have rest potentials much higher than those of sulphides. The value for pyrolusite is 1.20 V vs. SHE. Therefore, reactions of iron pyrites and manganese dioxides very often may be electrochemical in nature. Wadsworth has treated elaborately the leaching behaviour of metal sulfide according to the electrochemical theory. Equation (1.32) is the Butler-Volmer equation commonly applied to electrochemical rate process.

\[ I = K_a z_a C_a e^{\beta FE/RT} - K_c z_c C_c (1-\beta) FE/RT \]  

Where, \( I \) is the net current density, i.e., \( I_a + I_c \)

\( K_a, K_c \) = Anodic and cathodic rate constants in the absence of over potential.

\( Z_a, Z_c \) = Total number of electrons transferred in the anodic and cathodic processes

\( \beta \) = Transfer coefficient

\( F \) = Faraday number

\( E \) = Mixed potential

\( R \) = Universal gas constant

\( T \) = Absolute temperature

\( C_a, C_c \) = Concentration terms.
Manganese dioxide in its pure form dissolves sparingly in dilute sulphuric acid solutions. The possible reactions are as follows:

\[
\begin{align*}
\text{MnO}_2 + 4\text{H}^+ + 2e^- & \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \\
\text{MnO}_2 + 4\text{H}^+ + \text{e}^- & \rightarrow \text{Mn}^{3+} + 2\text{H}_2\text{O} \\
\text{Mn}^{4+} + 2\text{H}_2\text{O} & \rightarrow \text{MnO}_2 + 4\text{H}^+ \\
\text{MnO}_2 + \text{Mn}^{2+} + 4\text{H}^+ & \rightarrow 2\text{Mn}^{3+} + 2\text{H}_2\text{O}
\end{align*}
\]  

(1.33) (1.34) (1.35) (1.36)

In strongly acid solutions and depending on Mn(II) concentration, the electrode potential of MnO₂ rises above that of oxidation of water to oxygen and thus oxygen is formed:

\[
\text{MnO}_2 + 2\text{H}^+ \rightarrow \text{Mn}^{2+} + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2
\]

(1.37)

The rate of this process being controlled by oxygen over-voltage. Most of the manganese dioxide samples both natural and synthetic contain manganese(III) in some form or the other. In sulphuric acid this manganese (III) is leached out first according to the equation (1.38).

\[
(\text{MnO}_2)_{2n-3}\cdot\text{MnO(OH)}_{4-2n} \cdot n\text{H}_2\text{O} + \frac{\%}{2}(4-2n)\text{H}^+ \rightarrow \text{MnO}_2 + (4-2n)\text{Mn}^{3+} + 2(4-2n)\text{H}_2\text{O}
\]

(1.38)
However, in the presence of reducing agents, manganese dioxide gets reduced forming either manganese (III) or manganese (II) depending upon the nature of the reductant. Several reports have appeared recently on the leaching of manganese ore and ferromanganese ocean nodules in aqueous medium using reductants like iron(II) sulphate, sulphur dioxide or sulphurous acid. Manganese sulphate is manufactured by saturating suspension of high grade pyrolusite in dilute $H_2SO_4$ (15%) with $SO_2$. Manganese dithionate ($MnS_2O_6$) is formed and is decomposed by injecting steam into the solution.

\[
MnO_2 + 2H_2SO_3 \longrightarrow MnS_2O_6 + 2H_2O \quad \ldots \quad (1.39)
\]

\[
MnS_2O_6 \longrightarrow MnSO_4 + SO_2 \quad \ldots \quad (1.40)
\]

Reduction of manganese dioxide by sulphurous acid has been studied by a number of investigators. Henn et al. (1968) discussed some processes on recovery of manganese from manganese oxide ore using aqueous sulphur dioxide as reducing agent. They reported that above $pH$ 3.5 insoluble manganese sulphite was formed.

\[
Mn^{2+} + H_2SO_3 \longrightarrow MnSO_3 + 2H^+ \quad \ldots \quad (1.41)
\]

Below $pH$ 3.5 manganese dithionate ($MnS_2O_6$) was formed (reaction 1.39) and still lowering of $pH$ led to formation of manganese sulphate.
Back et al.\(^{99}\) (1952) reported also lowering of pH led to decrease in dithionate formation when they studied reduction of MnO\(_2\) with aqueous sulphur dioxide in presence of air. They further reported that dithionate formation was reduced with the increase of stirring rate. Meyer and Schramm\(^{100}\) (1923) reported the formation of manganese sulfate and manganese dithionate through the intermediate formation of manganese sulphite, Mn\(_2\)(SO\(_3\))\(_3\) and suggested the following stoichiometries for reduction of manganese dioxide by aqueous sulphur dioxide.

\[
\text{H}_2\text{SO}_3 + \text{MnO}_2 \rightarrow \text{MnSO}_4 + \text{H}_2\text{O} \quad \ldots \quad (1.42)
\]

\[
2\text{MnO}_2 + 4\text{SO}_2 (\text{aq.}) \rightarrow \text{Mn}_2(\text{SO}_3)_3 + \text{SO}_3 (\text{aq.}) \quad (1.43)
\]

\[
\text{Mn}_2(\text{SO}_3)_3 + \text{SO}_3 (\text{aq.}) \rightarrow \text{MnSO}_4 + \text{Mn}_2\text{O}_6 + \text{SO}_4^{2-} \quad (1.44)
\]

Klaus et al.\(^{101}\) (1983) reported that a recovery of 95% of manganese was achieved by passing sulphur dioxide to a suspension of pyrolusite containing manganese ore at pH 4.2. Partial pressure of oxygen is an important factor affecting the dissolution of manganese dioxide in aqueous sulphur dioxide. Dixit and Raisoni\(^{102}\) (1987) investigated the leaching of manganese from manganese dioxide samples by aqueous sulphur dioxide solution in an autoclave. They reported that the increase of
the oxygen pressure in the autoclave shifts the solution potential towards more oxidizing conditions and makes more difficult the reduction of manganese dioxide. It is known\textsuperscript{103} that MnO\textsubscript{2} is stable above a potential of 1.24 V. An oxygen pressure of 11.15 bar shifts the potential to a value above 1.24 V and MnO\textsubscript{2} becomes stable.

Dixit and Raisoni\textsuperscript{102} (1987) reported the rate equation (1.4) was valid for their experimental data of manganese leaching.

\[ 1 - \frac{3}{2} \alpha - (1 - \alpha)^{\frac{3}{2}} = kT \quad \ldots \quad (1.4) \]

Miller and Wan\textsuperscript{104} (1983) investigated the dissolution of polymetallic ocean nodule in aqueous sulphur dioxide solution and reported that primarily the dissolution was controlled by the electrochemical reaction at the surface of the solid and the rate equation (1.3) was fitted for their experimental data.

\[ 1 - (1 - \alpha)^{\frac{3}{2}} = kT \quad \ldots \quad (1.3) \]

This idea of diffusion controlled process was supported by other observations like the independence of reaction rate from stirring speed, an apparent activation energy of 8.6 Kcal/mole, the inverse first order relationship between the rate constant k and the initial particle

\[ \text{initial particle} \]
diameter, etc.. They postulated the overall electrochemical reaction as equation (1.45).

\[ \text{MnO}_2 + 2\text{HSO}_3^- \rightarrow \text{Mn}^{2+} + 2\text{HSO}_4^- + 2e \]  
(1.45)

The cathodic half cell reaction would be dissolution of manganese while the anodic half cell would be the oxidation of \( \text{HSO}_3^- \) ion.

\[ \text{MnO}_2 + 4\text{H}^+ + 2e \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \ldots \]  
(1.45c)

\[ \text{HSO}_3^- + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{HSO}_4^- + 2e \ldots \]  
(1.45a)

In another work Raisoni and Dixit (1988) investigated the leaching of manganese ore with aqueous sulphur dioxide in a one liter cylindrical glass reactor and studied the effect of stirring rate, particle size, \( \text{SO}_2 \) concentration and temperature. They reported that the rate data for manganese dissolution fitted the equation (1.4) very well. Diffusion through the siliceous layer appeared to be the rate controlling process.

Pahlman et al. (1988) performed manganese ore heap leaching with aqueous sulphur dioxide and achieved above 90% manganese recovery. They reported that the leaching rate was dependent on the penetration rate of solution through the ore porosity.
Studies on reduction leaching of manganese ore using iron (II) sulphate as reducing agent have also been reported. Levan et al. (1964) investigated leaching of manganese from oxide ores using both ferrous sulfate and pickle liquor (from galvanizing plants containing ferrous sulfate and sulphuric acid). The oxidation reduction reaction they predicted for the pickle liquor interaction is given by the equation (1.46).

\[
\text{MnO}_2 + 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \rightarrow \text{MnSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} \quad (1.46)
\]

Extraction of manganese from the ore was quite rapid at temperature as low as 70°C and as much as 77 per cent of manganese was dissolved after 30 minutes contact time. Good extraction of manganese also was obtained with ferrous sulphate solution alone. The reaction is given by the equation (1.47).

\[
\text{MnO}_2 + 2\text{FeSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{MnSO}_4 + \text{Fe(OH)}_3 + \text{Fe(OH)SO}_4 \quad (1.47)
\]

Kishnan Nair (1974) reported a process of preparation of pure MnSO₄ from pyrolusite containing manganese ore using spent pickling liquor as reducing agent. Asotoff (1976) also reported a similar process for preparation of pure MnSO₄·4H₂O and MnO₂. Agladze et al. (1983) studied the kinetics of reduction.
of manganese dioxide by iron (II) and reported that the reaction was diffusion controlled. The activation energy calculated was 10.99 KJ/mole.

Whalley et al.\textsuperscript{111} (1957) and also Thomas and Whalley\textsuperscript{41} (1958) reported that pyrite (FeS\textsubscript{2}) can be utilised for preparation of a solution having the same composition like pickle liquor and thus, can be used for manganese leaching. FeS\textsubscript{2} reacts with oxygen in presence of water as follows:

\begin{equation}
\text{FeS}_2 + 3\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{FeSO}_4 + \text{H}_2\text{SO}_4 \quad (1.10)
\end{equation}

FeSO\textsubscript{4} in acid solution reacts with MnO\textsubscript{2} as in equation (1.46). This work was cited by Henn et al.\textsuperscript{98} (1968) in preparing a list of processes for manganese ore leaching. Cornelius and Woodcock\textsuperscript{112} (1958) investigated the pressure leaching of manganese ore with pyrite and reported reactions (1.10) and (1.46) to be taking place. The optimum conditions reported for the extraction of manganese were a temperature of 140°C, an oxygen partial pressure of 25 to 90 and a mole ratio of MnO\textsubscript{2} to FeS\textsubscript{2} of 1.0. Addition of H\textsubscript{2}SO\textsubscript{4} helped in raising of MnO\textsubscript{2} to FeS\textsubscript{2} ratio. Lo et al.\textsuperscript{113} (1985) investigated the use of manganese dioxide for the oxidative leaching of sphalerite (ZnS) from a sphalerite and pyrite containing sulphide ore and reported that as the
oxidation progressed more and more pyrite was oxidised compared to the sphalerite. Sakairi (1966) achieved manganese extraction of about 90% by suspended particle leaching of manganese ore with pyrite under the condition of temperature 150°C, $\text{FeS}_2/\text{MnO}_2$ molar ratio 4 and acid concentration of 0.2N $\text{H}_2\text{SO}_4$. The kinetic study of $\text{MnO}_2$ leaching in dilute sulphuric acid solution using pyrite as reductant has been reported by the author. The dissolution rate of manganese ore containing $\text{MnO}_2$ is independent of the speed of stirring but dependent upon temperature, particle size, specific surface area of manganese ore, acid concentration and amount of pyrite. An activation energy of 43.6 KJ/mole has been obtained and the inverse relation of particle diameter with dissolution has been established.

SCOPE OF THE WORK:

It is seen from the information presented so far that enough work has been carried out on the sulphatization roasting and reduction leaching of manganese dioxide using some or the other reductant. But literature, particularly, on the use of iron pyrites for these processes is very much limited. Information on reaction mechanisms and rate characteristics of both sulphatization roasting and reduction leaching process are not available.
Therefore, the objective of this study is to investigate (i) sulphatization roasting and (ii) reduction leaching of manganese dioxide using iron pyrites as the sulphatizing and reducing agent. For each process, attempts have been made to establish the reaction stoichiometries and paths of the reaction (sulphatisation and leaching) curves. The mechanisms and rates of reactions involved in these processes are dependent on several physical and chemical characteristics of reacting materials. Chemical analysis, XRD study, optical microscopic study and measurements of packing density, specific gravity and specific surface area were utilised to assess the effects of physical and chemical characteristics of reactants on the rate of formation of manganese sulphate.

The study on sulphatization roasting of manganese dioxide with pyrite involves the following steps for establishing reaction mechanism and kinetics.

(a) Roasted products of different temperatures have been characterised by total chemical analyses and XRD study, (b) effects of different variables such as temperature, reaction time, particle size,
surface area, packing density, etc., on sulphatization of manganese have been studied by monitoring the water soluble manganese sulphate after roasting, and (c) sensitive thermal analysis techniques have been applied to obtain information on weight changes and heat effects accompanying the reactions.

Reduction leaching was studied in a dilute sulphuric acid medium. Mechanism and rate characteristics of aqueous phase reactions were determined by monitoring manganese sulphate and iron sulphate leached into the solution in the suspended particle leaching of MnO₂ and pyrite mixture. Effect of different reaction parameters such as temperature, concentrations of reactants, agitation rate, particle size, bulk density, specific gravity and surface area upon the leaching were studied. Measurements of electrochemical parameters for manganese dioxide and pyrite electrodes have been undertaken to obtain Evan's diagram. Corrosion and mixed currents from Evan's diagrams were compared with Manganese and iron leaching data of manganese dioxide and pyrite pellets. Galvanostatic polarisation curves for manganese dioxide, pyrite and also for Fe⁺⁺/Fe⁺⁺⁺ couples were plotted with the help of a potentiostat. Thus, a combined investigation on suspended particle leaching, pellet leaching,
electrochemical measurements and galvanostatic polarisation curves gave a concrete picture of reaction stoichiometries and rate characteristics of reduction leaching process of manganese dioxide with iron pyrite.