CHAPTER 1
PROLOGUE TO BIOLEACHING
Mines are the source of treasury; from treasury comes the power of Nation. Ever since the dawn of civilisation, minerals and their derivatives – metals have played an indispensable role in the progress of mankind. The history of mankind from time immemorial shows intimate and inalienable relationship with minerals and metals. Their progressive preponderance in human life over a period of time, in due recognition of their inseparable and obstructive impact of the quality of life is well high discernible (1-3).

In this modern industrial era, few people stop to realise the extent to which we have become dependent upon materials of mineral kingdom. Minerals have revolutionised the present age. In all walks of life, it is the mineral, which draws the wheels of civilisation (1, 4, 5). Human civilisation is based upon the seven metals known as the ‘metals of antiquity’, which are listed in Table 1.1 (6, 7, 8).

This shows that process metallurgy is one of the oldest sciences. Its history can be very well traced back to 6000 BC. Currently there are 86 known metals. But before the 19th century, only 24 of these metals had been discovered and, of these 24 metals, 12 were discovered in the 18th century. Therefore, from the discovery of the first metals – gold and copper, until the end of the 17th century, for some 7700 years, only 12 metals were known (7-10).

Metals in the minerals are generally present as oxides, carbonates or sulphides. The minerals in which the metals are sufficiently concentrated and form commercial sources of desired metals are called ores (11). A process applied to obtain pure metals after excavation of ore from the mines is referred to as ‘Mineral Processing’ (12). The conventional mineral processing or metal recovery from the high-grade ores and concentrates can be categorised as Pyrometallurgy and Hydrometallurgy. Pyrohydrometallurgy includes the combination of both the above processes (13-15). The raw ore obtained after mining always has a mixture of metals along with other wastes, which are referred to as ‘gangue’. Each ore body is
Table 1.1: Metals of Antiquity.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Discovery time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>6000 BC</td>
</tr>
<tr>
<td>Copper</td>
<td>4200 BC</td>
</tr>
<tr>
<td>Silver</td>
<td>4000 BC</td>
</tr>
<tr>
<td>Lead</td>
<td>3500 BC</td>
</tr>
<tr>
<td>Tin</td>
<td>1750 BC</td>
</tr>
<tr>
<td>Iron</td>
<td>1500 BC</td>
</tr>
<tr>
<td>Mercury</td>
<td>750 BC</td>
</tr>
</tbody>
</table>
unique; thus no two mineral processing plants are identical though some similarity may exist (12, 16).

Conventional pyrohydro metallurgical process for metal recovery is a multi-step complex process (12, 17-20), which can be outlined in a simple way as described in Figure 1.1. These processes have several demerits including different environmental pollution, which is produced at each stage of the process. The major limitations of this technology are as follows:

- It can only be applied to high-grade ores and pure concentrates,
- requires preferably high temperature and pressure,
- requires high input of energy,
- requires sophisticated instrumentation,
- investment of high capital cost for plant erection,
- is not viable to small reserves,
- is not a method of choice for complex ore or multimetal concentrate,
- produces huge amount of low-grade ore waste, tailings and other pollution (13-21).

These drawbacks of the process, continuous depletion of the mineral resources day by day both from the viewpoint of quality and quantity, reduction in the availability of new resources of minerals as well as the increased awareness towards environmental pollution and its impacts have imposed the planners to look for:

- better utilisation of the available resources,
- waste recovery,
- resource management,
- extend the life of deposits/resources for future mankind and
- a search for an alternative technology for the metal recovery from complex ore and concentrate (3, 22-25).

In the past few years, 'microorganisms mediated metal extraction' has been receiving increased attention because the technology has the potential to alleviate many of the problems being experienced by the mining industry
Figure 1.1: Typical flowchart for pyrometallurgical processes.
and may provide, in selective cases, an energy-saving alternative to the pyro-
and hydrometallurgical processes (26-28).

**Bioleaching** is a simple, effective, clean and economically viable supplementary technology to the conventional process (29-34). The origin of extractive hydrometallurgy goes back to a very early time, when people began melting certain rocks and minerals to obtain the new material known as metals. This resulted in the search for these stones and their systematic collection from the surface of the earth. The first example reported of ancient mining by a Greek naturalist and physician around 166 AD, concerned several copper mines of Cyprus (26, 34, 35). Permeable copper bearing rock was leached with surface water and the copper-sulphate-containing solution was collected, and from this solution, copper was recovered by iron precipitation (34, 36).

More than 1500 years after this early *in-situ* leaching operation, copper heap leaching on a commercial scale at Rio Tinto Mine, Spain was established (37, 38). Metal solubilization processes were believed to be solely chemical reactions mediated by water and oxygen until 1947, when Colmer and Hinkle demonstrated the bacterial catalysis of iron oxidation and sulphuric acid formation in mine waters (39-41). However, the first report, as early as in 1920s, the oxidation of zinc sulphide by unidentified sulphur oxidising microorganisms was narrated, suggesting a biological method for an economical utilisation of low-grade zinc sulphide ores (26, 42). With the recognition of the interactions between the biosphere and the lithosphere, a scientific field for metal extraction opened; which is currently referred to as Biohydrometallurgy (34).

Bioleaching is a branch of biohydrometallurgy (34) and can be defined as the ability of the microorganisms to attack and dissolve mineral deposits, usually water-insoluble metal sulphides or oxides, to water-soluble metal sulphates. Bioleaching process occurs naturally wherever suitable
conditions are found for the growth of the ubiquitous bioleaching bacteria (31).

Biohydrometallurgy is a new and promising technology, useful for obtaining valuable metal compounds from ores or for detoxifying industrial waste products containing metals. It includes

- the solubilization of metals contained in ore, solid residues and others by the aid of microorganisms,
- the recovery of these metals as salts and
- the subsequent purification steps (27, 33, 36).

After the 1992 Earth summit in Rio de Janeiro, the concept of sustainable development has become very popular and its importance has been recognised. In this context, biohydrometallurgical processes became the method of choice for metal recovery. These processes have a high relevance for cleaner technology, recycling of materials and waste minimisation, thus will become a very important subject of research in the future (36, 43). The advantages of biomining processing are

- simple and effective process,
- can work at ambient temperature and pressure,
- economically viable for extraction of metals from low-grade or waste ores,
- can be proved a method of choice for the extraction of metals from bulk complex concentrates,
- can work for refractory ores,
- low energy input and capital cost as compared to pyrohydrometallurgical process,
- can be used for selective leaching,
- low to moderate capital investment,
- processing plant can be built in the immediate vicinity of the ore deposit, thus saving transport cost,
- low operating cost,
+ secondary recovery of metals possible that otherwise are discarded,
+ flexible for the treatment of mineral resources with a variety of metals
  and in variable concentrations,
+ environment friendly process (22, 27, 33, 36).

Microorganisms are the backbone for the biomining activity. A wide
range of bioleaching bacteria have been isolated from industrial leaching
operations or from sites of natural leaching that are capable of attacking
mineral sulphides (44, 45). On the basis of their preferred growth
temperatures, these organisms are divided into two major groups –
Mesophiles and Thermophiles (46, 47).

The most important mesophiles are *Thiobacillus ferrooxidans*,
*Thiobacillus thiooxidans*, *Leptospirillum ferrooxidans*, *Chromobacterium
violaceum*, *Micrococcus lactilyticus*, *Metallogenium* spp., *Hyphomicrobium*
spp., *Desulphovibrio* spp., and *Desulphotomaculum* spp. (46, 48-51). All
these microorganisms play a very critical role in the solubilization of metals
from ores and concentrates. The most studied and commercially exploited
‘microminers’ i.e. *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans* and
*Leptospirillum ferrooxidans* are highly acidophilic, obligate autotrophs and
grow optimally at temperatures of 25-35° C and at pH range of 1-3 (45, 52).

The important extreme and moderate thermophiles are *Sulfolobus*
*Thiobacillus caldus*, *Galdieria sulphuraria* etc. (51, 53-55).

**Mechanism of bacterial leaching**

Huge literature is available regarding bacterial activity in metal
solubilization. Three mechanisms are generally involved during bioleaching
of sulphide minerals, namely, direct, indirect and galvanic conversion (34,
56, 57). The mechanisms of metal extraction process are summarised in
Figure 1.2.
Figure 1.2: Bioleaching mechanisms.

**Indirect mechanism due to $O_2$**

**Direct mechanism**

**Major limitations in bioleaching**
The 'direct' mechanism (now renamed as 'contact leaching') (58) of sulphide mineral oxidation requires intimate contact between mineral and acidophilic microorganisms such as *Thiobacillus ferrooxidans* and are known to adhere strongly and selectively to the sulphide moiety in a mineralogical milieu (17, 34, 51, 56). Strong mineral oxidation is envisaged to proceed by direct oxidation by attached microorganisms (57-66). It can be described by the simplified reactions for any bivalent metal (M) and for chalcopyrite (67).

\[
\text{Thiobacillus ferrooxidans} \\
\text{MS} + 2\text{O}_2 \rightarrow \text{MSO}_4
\]

\[
2\text{CuFeS}_2 + 8\frac{1}{2}\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{CuSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}
\]

The 'indirect' mechanism of sulphide mineral degradation focuses on the role of soluble ferric iron in abiotic oxidation. The following reaction represents the indirect leaching mechanism (67, 68).

\[
\text{MS} + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{MSO}_4 + 2\text{FeSO}_4 + \text{S}^0
\]

\[
\text{CuFeS}_2 + 2\text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{CuSO}_4 + 5\text{FeSO}_4 + 2\text{S}^0
\]

In the ‘indirect’ mechanism, the prime role of acidophilic iron bacteria is to regenerate ferric iron (37, 62, 63, 69-73):

\[
\text{Fe}^{2+} \xrightarrow{\text{Biological}} \text{Fe}^{3+} + \text{e}^-
\]

Biological oxidation of elemental sulphur (e.g. by *Thiobacillus ferrooxidans* or *Thiobacillus thiooxidans*) has the dual advantage of generating acidity (thereby helping to maintain ferric iron in solution) and removing sulphur which may otherwise accumulate and impede mineral dissolution.

\[
\text{S}^0 + \text{H}_2\text{O} + 1\frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{SO}_4
\]

Both the direct and indirect mechanisms are thought to operate concurrently (74), for example, during biological dissolution of pyrite, microorganisms attached to the mineral may oxidise the mineral directly as
Biological

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

and the ferrous iron so formed will be oxidised by both attached and free swimming iron oxidisers, thereby generating ferric iron which will oxidise pyrite indirectly. Recently this has been referred as ‘co-operative leaching’ during which attached and free bacteria carry out symbiotic activity (58).

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

Altogether in a classical way, bioleaching is based on the interaction of biological and chemical oxidation processes. Particular importance must be attributed to the cycle of ferrous and ferric iron. In nature and in technical application both mechanisms, the direct and the indirect leaching, undoubtedly occur in concert (34, 58, 63, 74). Still the details regarding the mechanisms of bioleaching is not clear.

‘Galvanic interaction’ is an inherent phenomenon in mix-sulphidic minerals, which operates automatically in a heterogeneous system or wherever two or more different environment coexist (34, 57, 75-80).

The role of galvanic interactions in the bioleaching of mixed sulphide minerals has been reported extensively (56). Minerals with a comparatively lower rest potential value behave anodically and undergo dissolution (oxidation) whereas the mineral with the higher rest potential value acts as a cathode at which reduction of oxygen occurs (68). The electrochemical reactions involved are given below (56):

Anodic reaction on active sulphide sites:

\[ \text{MS} \rightarrow \text{M}^{2+} + \text{S}^0 + 2\text{e}^- \], where M is a bivalent metal.

Cathode oxygen reduction on noble mineral:

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

Thus, bioleaching of polymetallic sulphide minerals is a complex process where bacterial, chemical and galvanic oxidation processes occur simultaneously (81).
During the last 25 years, bioleaching of minerals has opened up new opportunities for extractive metallurgy and bioextraction processes are now practised in the copper and uranium industries, especially for the treatment of low-grade ores in form of heap, dump and in-situ leaching (82-84). On the other hand, reactor leaching is getting popularity for the treatment of refractory gold ores (63, 81, 85).

Major bioleaching processes used world wide for the production of metals comprise of production of copper, uranium and gold. The overview of these metal productions by biohydrometallurgical means is summarised in the forth-coming sections.

**Bioleaching of copper**

Nowadays, the extraction of copper from low-grade ores by microbiological leaching is carried out on an enormous scale. Bioleaching of copper from chalcopyrite, chalcocite and covallite have been practised successfully using large-scale techniques like in-site, heap and dump leaching at various mine sites (86, 87). Extraction of copper from low-grade ores using microorganisms has been operating for far longer time than any other such application. Since the 1950s, biological copper leaching has been practised in many countries, including the USA, the former Soviet Union, Chile (currently the major centre for bioleaching of copper ores), Australia, England, Japan, Romania and Spain (35, 70, 82, 88-91). A major reason for the emergence of bioleaching of copper-containing ores is that high-grade ore bodies have become increasingly rare, so that costs involved with conventional extraction for transporting, grinding and smelting of ores have continued to increase (70). Merson (1992) quoted costs of between $60 and $90 per pound of copper recovered by smelting, compared to that by bioleaching which is about $30. In addition, environmental concerns about polluting gas emissions (sulphur dioxide etc.)
from smelter stacks have also increased. One ton of copper smelting produces about two tons of SO\(_2\) gas (70, 92).

Exact numbers on how extensively bioleaching is used are not available. In the 1970s, the largest plant for microbial leaching was that for dump leaching of the Kennecott Copper Corporation at Bingham, UT, USA. The contents of the dumps stored there were estimated to be more than 3.6 x 10\(^9\) tonnes and about 200 tonnes.d\(^{-1}\) of copper was recovered by bioleaching (63). It has been estimated that in 1984, copper valued at US $350 million and representing 10% of US copper production was recovered by bioleaching (Gorham International Inc.). According to the estimation by Torma, the actual figure was higher, between 18 and 25%, for copper production (93, 94). Perhaps 3.3 x 10\(^7\) tonnes of copper is located in mine dumps in the western US. It has been estimated that at least 15-30% of world production or 2-3 Mt of copper are bioleached annually (36). Chile is presently the world's major copper producing country with copper reserves of 1.5 x 10\(^8\) tonnes of which 4.7 x 10\(^7\) tonnes (32%) are contained in ores of a grade too low for conventional technology to be profitable (31). It is expected that within the next years, several industrial applications of bacterial leaching will be operated, yielding 2.5 x 10\(^5\) tonnes of cathodic copper per year which will be equal to about 16% of the present total copper production in Chile (29, 63). Presently Chile (Quebrada Blanca) is producing 7.5 x 10\(^4\) tonnes of copper annually by bioleaching technique (63). Some commercial bacterial leaching operations for copper solubilization are documented in Table 1.2 (82, 83).

Bioleaching of uranium

Copper and uranium leaching are the examples of successful commercial application of biohydrometallurgy (95). Uranium, a nuclear metal occurs essentially as uraninite (UO\(_2\)) and pitchblende (U\(_3\)O\(_8\)) in nature and the ores are of very lean grade (less than 0.1%). Tetravalent uranium is
Table 1.2: Commercial bacterial leaching operations for copper.

<table>
<thead>
<tr>
<th>Mine</th>
<th>Process</th>
<th>Production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gundpowder's Mammoth Mine, Australia</td>
<td>in situ</td>
<td>1,000 t.a⁻¹</td>
</tr>
<tr>
<td>Blue Bird Mine, USA</td>
<td>Heap</td>
<td>6,800 t.a⁻¹</td>
</tr>
<tr>
<td>Baghdad, USA</td>
<td>Dump</td>
<td>13,600 t.a⁻¹</td>
</tr>
<tr>
<td>Kosaka Mine, Japan</td>
<td>in situ</td>
<td>800 t.a⁻¹</td>
</tr>
<tr>
<td>Rio Tinto, Spain</td>
<td>Dump</td>
<td>8,000 t.a⁻¹</td>
</tr>
<tr>
<td>Lo Aguirre, Chile</td>
<td>Heap</td>
<td>16,000 t.a⁻¹</td>
</tr>
<tr>
<td>Mt. Leyshon, Australia</td>
<td>Heap</td>
<td>1,370 t.d⁻¹</td>
</tr>
<tr>
<td>Cerro Colorado, Chile</td>
<td>Heap</td>
<td>16,000 t.d⁻¹</td>
</tr>
<tr>
<td>Girilambone, Australia</td>
<td>Heap</td>
<td>2,000 t.d⁻¹</td>
</tr>
<tr>
<td>Ivan-Zar, Chile</td>
<td>Heap</td>
<td>1,500 t.d⁻¹</td>
</tr>
<tr>
<td>Quebrada Blanca, Chile</td>
<td>Heap</td>
<td>17,300 t.d⁻¹</td>
</tr>
<tr>
<td>Andacollo, Chile</td>
<td>Heap</td>
<td>10,000 t.d⁻¹</td>
</tr>
<tr>
<td>Dos Amigos, Chile</td>
<td>Heap</td>
<td>3,000 t.d⁻¹</td>
</tr>
<tr>
<td>Zaldivar, Chile</td>
<td>Heap</td>
<td>20,000 t.d⁻¹</td>
</tr>
</tbody>
</table>
acid insoluble and only its hexavalent form is readily soluble in sulphuric acid solutions. Hence it becomes essential to oxidise the naturally occurring uranium to the Hexavalent state before resorting to leaching (56, 95). Tetravalent uranium is oxidised to U(VI) by soluble ferric iron, produced by acidophilic iron oxidising bacteria by the indirect mechanism (70).

Commercial application of bioleaching of uranium from low-grade ores has been practised since the 1960s. Best known are the in-situ leaching operations in the underground uranium mines in the Elliot Lake District of Canada including the Stanrock, Milliken and Denison mines (95). At that time, the annual production of uranium from the Stanrock mine was about $5 \times 10^4$ Kg $U_3O_8$ whereas $6 \times 10^4$ Kg $U_3O_8$ was produced in the Milliken mine after improvement of the leaching conditions. In the beginning of the 1980s, a distinct drop in uranium production occurred. In 1984, Denison mines started new activities and in 1988-90, flood-leaching stopes were in various stages of operation or in preparation. Around 347 tons of uranium with a value of over US $25$ million were produced from this leaching operation (31, 95). With the present reduction in world demand for uranium, the prices are at a low level and uranium extraction is now less significant than in earlier decades (31, 63, 70).

Bioleaching of gold

Gold generally occurs either in elemental form or alloyed with silver (96). Gold in ‘free milling ores’ is readily liberated by crushing and grinding of ore; followed by a variety of alternative recovery techniques. Gold contained in ‘base metal ores’ is generally recovered during conventional smelting and refining operations as a by-product metal. However, of increasing importance are ‘refractory’ ores, in which the precious metal is finely disseminated within sulphide minerals, which are usually pyrite ($FeS_2$) and arsenopyrite ($FeAsS$) (37, 97, 98). In conventional mineral processing, gold is extracted with cyanide as a water-soluble complex, followed by
absorption by activated carbon, elution, and electro-winning. In refractory ores, the efficiency of gold extraction tends to be low because of cyanide consumption by other components in the ore (mainly FeS₂ and FeAsS). Bacterial pre-treatment by oxidative dissolution of pyrite and arsenopyrite usually increases gold recovery upon subsequent cyanidation (99-101). During the past 10 years, biological processes have been adopted on a commercial scale for the oxidative pre-treatment of gold-containing FeS₂ and FeAsS concentrates and several tank leaching operations are being run in South Africa, Brazil and Australia (37, 40, 63, 96, 102).

The pioneer plant at the Fairview mine (General Mining Union Corporation-Gencor), South Africa, established in 1984 treats a pyrite/arsenopyrite concentrate at a rate of 35 tonnes.d⁻¹. The process achieved about 95% gold recovery by pre-treatment with bacterial leaching followed by cyanidation as opposed to pyrometallurgical process where only 35% recovery was obtained (101, 102).

A biooxidation plant, Ashanti gold mines in Ghana, constructed during 1994, has a capacity to treat 1000 tons of gold-bearing concentrate per day (60).

Six commercial scale plants have been commissioned for biooxidation pre-treatment of sulphidic refractory gold concentrates, which are listed in Table 1.3 (82, 83). Several pilot plants are in operation e.g. New Mount Mining (Nevada, USA; 600 t heap), Harbour Lights (Australia; 40 t.d⁻¹), Sao Bento (Brazil; 150 t.d⁻¹), Vall Reefs Gold Mine (South Africa; 20 t.d⁻¹), BRGM (France; 100 Kg.d⁻¹), BIOX® - GENMIN (South Africa) and Equity Pilot Plant (British Columbia, Canada; 2 t.d⁻¹) (31, 56, 96, 102-106).

Because the price of gold has risen, many mineral companies are now taking a second look at deposits that were once considered uneconomical. Bioleaching offers a new low-cost alternative for oxidising these refractory ores (60).
Table 1.3: Commercial biooxidation plants treating refractory gold concentrate.

<table>
<thead>
<tr>
<th>Plant</th>
<th>Size (tonnes.d⁻¹)</th>
<th>Years in operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fairview, South Africa</td>
<td>10</td>
<td>1986 – 1991</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>1991 – Present</td>
</tr>
<tr>
<td>Sao Bento, Brazil</td>
<td>150</td>
<td>1990 – Present</td>
</tr>
<tr>
<td>Wiluna, Australia</td>
<td>115</td>
<td>1993 – Present</td>
</tr>
<tr>
<td>Ashanti, Ghana</td>
<td>1000</td>
<td>1994 – Present</td>
</tr>
<tr>
<td>Youanmi, Australia</td>
<td>120</td>
<td>1994 – 1998</td>
</tr>
</tbody>
</table>
Recent advances in bioextractive metallurgy have also opened the doors for metal extractions from complex sulphidic minerals. Metal recovery from such complex ore and bulk concentrates is equally important for the economical growth of nation. The possibility of such treatment and on going research activities in this field is summarised in next section.

Bioleaching of complex minerals

The depletion of high-grade mono-mineral ore deposits and increasing demands for base metals have led mining companies to consider exploiting multi-metallic and lean ores, which represents important resources of non-ferrous and precious metals. The complex ore is generally composed of chalcopyrite, galena, sphalerite, pyrite and/or pyrrhotite (107). Tin, arsenic and precious metals (gold and silver) are frequently present in the form of arsenopyrite. Of the numerous antimony minerals, stibnite, tetrahedrite and lead ores are the major sources of complex minerals as far as commercial extraction is concerned. Another complex mineral is the cobalt-nickel sulphide, which also represents a good source of non-ferrous metal. These minerals are often finely inter-grown with each other and with the pyrite matrix, other than with the gangue (34).

Metal extraction from complex ores and concentrates can be achieved pyrometallurgically or biohydrometallurgically. Pyrometallurgical processes for complex ores requires “selective floatation process”. To obtain individual concentrates from complex sulphide ores, a fine grinding step (or ultra grinding) is required to liberate the mineral species to be separated, which is an energy-consuming, expensive operation, necessitating skilled labour. So, flotation separation of complex sulphide ores into individual concentrates has been a difficult task, often due to the size of liberation and possible interactions among sulphide minerals (108, 109). Moreover, this solution is not satisfactory and economical, in practice, owing to the high costs of the differential flotation process, low flotation recovery and to the poor quality of
the resulting concentrates which hinder their access to the market (34, 108-110).

"Bulk flotation" shows significant advantages as contrasted with differential flotation in terms of less water and reagents consumption, higher metal recovery efficiency and less grinding cost. Inspite of these advantages, at present, the main difficulty lies in selecting an efficient, inexpensive and flexible leaching process (34, 110).

This situation prompted an examination of alternatives in arriving at an economically sound process to extract metal from finely inter-grown complex sulphide concentrates. In this respect, biohydrometallurgical process is considered as an interesting choice (34, 109, 110).

Biohydrometallurgical methods are currently used in commercial leaching processes for the recovery of copper, uranium and gold from sulphidic minerals (95, 96, 111). In the future, these processes will become important for zinc, nickel, cobalt and molybdenum from the complex ores (63, 112). ‘Combination processes’ involving an initial bulk flotation followed by selective leaching of certain sulphide minerals could prove attractive in the processing of refractory complex ores (56). It is of tremendous interest to explore if selectivity could be achieved in the leaching of multi-metal sulphides (81).

Bacterial leaching either of the run-of-mine ore or of a bulk metal sulphide concentrate appears promising. Production of the later usually involves a relatively coarse grind and is characterised by satisfactorily high recoveries (113-115).

Bacterial leaching has been found to be effective in the dissolution of several sulphide minerals. Possible selectivity for sulphide mineral oxidation of complex sulphides by bacteria depends on the following key factors:

♦ Galvanic interaction between different sulphide mineral species and presence of bacteria.
Prologue

- Bacterial attachment to selected sulphide mineral sites and direct microbial attack.

Application of bioleaching to the processing of complex sulphide such as the ores containing Pb-Zn-Cu-Fe, Cu-Ni-Mo-Fe and Cu-Ni-Fe metals is of great importance since flotation-beneficiation of these multi-metal ores to yield individual clean concentrates (for pyrometallurgical processes) is extremely difficult. A combination process would prove to be very efficient in these cases (56).

However, information concerning the bioleaching of multi-metal (complex) sulphides is limited. To date, experiments have been carried out only on a laboratory scale on complex sulphide run-of-mine ores, on mixed metal sulphide flotation concentrates and on synthetic mixtures of chemical grade base-metal sulphide and sulphites (34, 112, 117).

Bioreactor systems have been tested for direct bioleaching of copper and zinc concentrates. For zinc, higher than 90% recovery has been attained at a rate of about 0.4 Kg.m⁻³.s⁻¹. For copper, about 50% recovery has been reported at a rate of about 0.11 Kg.m⁻³.s⁻¹. These processes are not yet commercialised (34).

Recently in Spain (Rio Tinto Mine) IBES bioleaching plant of a copper-zinc sulphide concentrate is commissioned with a capacity of 10⁵ t.a⁻¹ concentrate. The operating cost was calculated to be about US $141 per ton of concentrate. It is a two-stage process and silver is used as a catalyst with an 8 and 10 h retention time. In this plant, 94% zinc and 95% copper was recovered (28, 118, 119). Market share of some metals obtained by bioleaching processes and comparison with world production is given in Table 1.4 (36).
Table 1.4: Comparison of production of some metals by bioleaching process with total world production.

<table>
<thead>
<tr>
<th>Metal</th>
<th>World production (Kt)</th>
<th>Year</th>
<th>Proportion obtained by biological leaching (%)</th>
<th>Process name</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>2.1</td>
<td>1992</td>
<td>20</td>
<td>BIOX, MINBAC</td>
<td>Gencor, South Africa</td>
</tr>
<tr>
<td>Copper</td>
<td>8925</td>
<td>1994</td>
<td>15-30</td>
<td>-</td>
<td>Phelps Dodge, USA</td>
</tr>
<tr>
<td>Nickel</td>
<td>900</td>
<td>1992</td>
<td>NA</td>
<td>BioNiC</td>
<td>Gencor, South Africa</td>
</tr>
<tr>
<td>Uranium</td>
<td>23.1</td>
<td>1993</td>
<td>10-15</td>
<td>BACFOX</td>
<td>Denison Mines, Canada</td>
</tr>
</tbody>
</table>

NA: Data not available.
Economics

Economical factors for commercial-scale leaching applications can be divided into capital costs associated with construction and operation costs. Operation costs includes the running of the process equipments and the supply of reagents, services and labour (120). They are comparable with those of competing technologies; however, capital costs are generally smaller. According to Barrett et al. (121), the capital costs depend on the methods of application, and increase in the order,

Dump < Vat ≤ Heap < Agitated reactor

Construction material and equipment are the major items affecting costs. Major equipment required for agitated bacterial oxidation processes includes conventional tanks with impellers to suspend the solids and disperse the air, compressors for air supply, thickeners for solid/liquid separation, and conventional slurry pumps for delivering and removing the slurry from the plant. The construction material needs to be acid-resistant, and also able to withstand temperatures of 30-50°C. In general, the technical equipment for bioleaching processes is less expensive than that required for physico-chemical processes. However, longer treatment times are frequently required for bacterial leaching processes, which partly offset this profit (122, 123). Another major capital cost in establishing a particular application is the services to support the process. In addition, except for the extracted metals, the process forms no saleable products. The acid generated is of low-grade quality and mostly contaminated with metals and salts. By-products contained in waste streams are normally not recoverable in an economical way (34, 36).

An economical profile was calculated for an old copper tailing in Chile containing between 0.18 and 0.26% copper (124). A total investment of US $20.5 million for the whole leaching process for a plant capacity of 16 t copper.d⁻¹ would have been necessary. The operation costs amount to
US $0.99 per Kg copper. The annual net present value represents US $2.11 million for a copper price of US $1.76 per Kg copper, and results in an internal rate of return of 14.2% (36).

Recovery of gold from ores could be increased by 2-13% if biotechnological methods were applied. In comparison to ore roasting, capital cost for industrial scale treatment plants are reduced by 12 – 20%, operating cost by 10% (125). Costs of US $4.3 per ton ore have been calculated for bacterial ore treatment compared to US $4.1 and US $4.5 for pressure oxidation and roasting respectively (36, 120, 126).

**Patent applications**

Only a few patents have been published concerning biohydrometallurgical processes. Approximately 15 patents with worldwide relevance are known to have been taken out since 1990. Most of the patents covering biological leaching process deal with the leaching of low-grade ore. Major patents are applied to the ore for extraction process of gold and copper. Only one patent was applied to zinc concentrate for the recovery of cadmium, copper and zinc through reactor process by MIM Holding Ltd., Brisbane, Australia (36).

**Indian scenario**

It is needless to say that the use of minerals from the rudest flint implement used 5,00,000 years ago to the latest precision tools and the world orbiting artificial satellites truly shaped the destiny of man (1-3). The mineral wealth of India is a gift of nature and being the home of a very ancient civilisation, has a rich heritage of mining and metallurgy dating back to the pre-Harappan period (4000 – 2000 BC). It was the only source of diamond for the world for over 3000 years and has a heritage of world’s
oldest zinc technology besides extensive and deep working of copper, lead, zinc etc. (2, 7-9).

However, very little attention was paid to the exploration of these mineral resources until independence (1). In the five decades since independence, India's minerals sector has demonstrated a remarkable growth rate and the value of mineral production has multiplied almost 480 times.

India's mineral resources are summarised in Table 1.5 (16, 127-129). Production of some minerals/metals of India for the year 1997 is given in Table 1.6 (6).

India now ranks 2nd in the resources of manganese ore, 3rd in barytes and iron ore, 4th in Chromite, bauxite and magnetite, 5th in coal and lignite in the world (4). A recent Price Water House report has identified India as the most promising mining location world-wide.

Besides a host of minor and atomic minerals, India produces 65 minerals including fuel, metallic and non-metallic mineral (130). Metals are strategic and the important role they play in the national economy both during peace and war can not be underestimated. It is well known that the prosperity of the country and the people is measured by the yardstick of the per capita of metal consumption they have. If we compare the per capita consumption of base metals in India with other industrially advanced countries abroad (Table 1.7), we come to the conclusion that we lag far behind in this field (4).

With a population of 960 million, India is consuming increasing amounts of most minerals. The usage is expected to rise by 6 to 9% annually for most metals. Even at present we are not self sufficient for most of our demand of metals. Present situation of production and demand of base metals in India is illustrated in Table 1.8 (5).
### Table 1.5: India’s mineral resources.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ore/mineral</th>
<th>Reserve (Mt)</th>
<th>Geographical distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Hematite</td>
<td>11,950</td>
<td>Bihar, Orissa</td>
</tr>
<tr>
<td></td>
<td>Magnetite</td>
<td>4,900</td>
<td>Karnataka, Goa, Madhya Pradesh</td>
</tr>
<tr>
<td>Manganese</td>
<td>Pyrulusite</td>
<td>370</td>
<td>Orissa, Bihar, Madhya Pradesh</td>
</tr>
<tr>
<td></td>
<td>Psilomelane</td>
<td></td>
<td>Maharashtrea, Karnataka</td>
</tr>
<tr>
<td></td>
<td>Brunite</td>
<td></td>
<td>Gujarat, Goa</td>
</tr>
<tr>
<td>Cobalt and nickel in copper mines</td>
<td>Sulphide ores</td>
<td>-</td>
<td>Uttar Pradesh, Rajasthan</td>
</tr>
<tr>
<td>Copper</td>
<td>Chalcopyrite</td>
<td>425</td>
<td>Bihar, Andhra Pradesh, Rajasthan, Outer Himalaya</td>
</tr>
<tr>
<td>Gold</td>
<td>Quartz reefs</td>
<td>30</td>
<td>Karnataka, Andhra Pradesh, Madhya Pradesh, Ladakh</td>
</tr>
<tr>
<td></td>
<td>arsenopyrite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>Bauxite</td>
<td>279.9</td>
<td>Bihar, Madhya Pradesh, Maharashtra, Gujarat, Kashmir</td>
</tr>
<tr>
<td>Uranium</td>
<td>Pegmatitic</td>
<td></td>
<td>Biha, Andhra Pradesh, Rajasthan</td>
</tr>
<tr>
<td></td>
<td>Monazite</td>
<td></td>
<td>Himalayas, East and west coast of India</td>
</tr>
<tr>
<td>Zinc</td>
<td>Sphalerite</td>
<td>107.1</td>
<td>Rajasthan, Kashmir, Sikkim</td>
</tr>
<tr>
<td>Lead</td>
<td>Galena</td>
<td>~ 100</td>
<td>Rajasthan, Andhra Pradesh, Tamilnadu, Orissa, Gujarat</td>
</tr>
</tbody>
</table>
Table 1.6: Production of some minerals/metals of India (1997).

<table>
<thead>
<tr>
<th>Minerals/metal</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>308 million tonnes</td>
</tr>
<tr>
<td>Oil</td>
<td>50 million tonnes</td>
</tr>
<tr>
<td>Iron ore</td>
<td>72 thousand tonnes</td>
</tr>
<tr>
<td>Aluminium</td>
<td>656 thousand tonnes</td>
</tr>
<tr>
<td>Copper</td>
<td>55 thousand tonnes</td>
</tr>
<tr>
<td>Zinc</td>
<td>154 thousand tonnes</td>
</tr>
<tr>
<td>Lead</td>
<td>96 thousand tonnes</td>
</tr>
</tbody>
</table>
Table 1.7: Per capita consumption and the current growth rate.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Per capita consumption (Kg)</th>
<th>Demand growth rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Developed countries</td>
<td>India</td>
</tr>
<tr>
<td>Copper</td>
<td>10</td>
<td>0.3</td>
</tr>
<tr>
<td>Zinc</td>
<td>3.5 – 6.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Lead</td>
<td>5.6</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Table 1.8: Demand and supply of base-metals (1997).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Tonnes per annum</th>
<th>Production</th>
<th>Demand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>64,000</td>
<td>300,000</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>176,000</td>
<td>226,500</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>85,500</td>
<td>97,000</td>
<td></td>
</tr>
</tbody>
</table>
As can be seen, that there is a huge gap between demand and supply of metals from domestic sources and hence are currently met by imports. In future, this gap will widen more if any alternate process is not developed.

Inspite of cheap labour, strong technological base, liberalised market and vast consumer base, there exists a wide gap between the existing potential and the potentials to be exploited for economic metal growth (131). The reason is India has a variety of untapped mineral resources, largely sub-surface and hidden due to lack of modern technology, adequate exploratory efforts and intensive mineral investigation (130). If we take the example of copper reserves of India, there are 205 deposits. All the reserves are scattered and none of the deposit identified so far can be termed as “World Class” deposit (132). Average copper content in Indian ore is about 1.0 to 1.5% while in other countries, it is to the tune of 2.5 to 3.5% (133). This means that the geometry of ore body in India is thin, lenticular and low dipping, as against massive in other countries and unfortunately, Indian ore predominantly comprises of chalcopyrite, which is difficult to be leached (132).

Looking towards these limitations and conditions, bioextraction technology holds great promise and practical significance in India. Bioleaching technology can be a ‘boon’ to a country like India where the low-grade mineral reserves are easily available and the warm climatic conditions favour the growth of the leaching organisms. Biological metal extraction processes have attained commercial acceptability world - wide. There is no reason why India should lag behind in adaptation to this technology.

The opportunities await in India in the field of bioextraction can be listed as

- Development of super strain.
- Generation of large amount of bacterial biomass.
- Modelling and optimisation of biomineral technology.
- Bioheap leaching.
• Extension of biogeotechnology to other non-ferrous metals.
• Biomineral beneficiation.
• Bioreactor to treat metal concentrates (56).

Biomineral processing holds great potential for India. The technology can be applied for both the existing process operations and newer unexploited deposits for the recovery of metal from non-ferrous refractory ores and concentrates. Although, many research efforts on various aspects of bioleaching of different types of Indian ores have been made, no fruitful commercial application of biotechnology has so far been made in the country. However, references are available in the literature on the biological extraction of zinc from sphalerite concentrate and ore (134-138), copper extraction from chalcopyrite (139-146) and gold from refractory gold ores and concentrates (108, 147-151). There are also reports on the bioextraction of copper, zinc and lead from polymetallic minerals and concentrates (17, 112, 152-154) and copper and nickel from bulk copper-nickel sulphide flotation concentrate (155, 156). Bioextraction process scaled up to 20 dm³ STR (51) for zinc extraction from sphalerite concentrate and the heap leaching was erected at Malanjkhand site for copper extraction from a lean grade ore (157-160). The role of galvanic interactions in the leaching of polysulphidic minerals has been well studied by Natarajan et al (79, 117, 161), which governs the kinetics of metal extraction from the polymetallic minerals. It was observed that adapted strains of *Thiobacillus ferrooxidans* were found to enhance the specific metal dissolution from bulk flotation concentrate (155, 156).

Under the program of culture collection and data bank development with respect to biohydrometallurgy in India, 207 potentially useful microorganisms were isolated from 60 copper and manganese mines in the country and were preserved with all the information on ores and cultures (24, 162). Manganese ore beneficiation and extraction process was studied under this program (163-165). Various growth aspects of *Thiobacillus*
ferrooxidans were studied in many Indian laboratories (117, 166-173). Few efforts were also made for the extraction of cobalt, lead, nickel, uranium and silica using diverse microbial cultures (15, 174-178). There are few research papers on the ecology of some Indian sulphidic mines and growth behaviour of metallurgically useful organisms on various substrates have been documented during the last two decades (179-184). Inspite of all these studies, enough data on polymetallic concentrate leaching are not available. There are few complex sulphidic mineral reserves in India such as Agnigundal, Andhra Pradesh; Ambamata mines, Gujarat and Rajpura-Dariba and Zawar Mines, Rajasthan which are neither fully exploited nor investigated. Even scantier data is available on bioleaching of Indian polymetallic concentrates. Each ore or concentrate is unique and the pulp minerology, quantity of individual minerals, their distributions in the particular concentrate or ore play a significant role in the dissolution of individual metals from the respective pulp.

India has well scattered small reserves of polymetallic ores. All these deposits are so small, that it is not possible to set up conventional recovery process at site. Transportation charges are very high due to long distances between the mine sites and processing plants. As mentioned earlier, it is very difficult to produce pure concentrate from polymetallic ore and the bulk concentrates are not good source for pyrometallurgical process. Thus it becomes imperative to look for some biotechnological means for processing such concentrates. Before execution of such processes, the detailed information/data is necessary with respect to both 'technical' and 'biological' aspects.

The technical aspects include:

• Improvement, modification and optimisation of the laboratory scale process used for the bioextraction of metals.
• Designing and modification of laboratory as well as pilot scale bioreactors.
Formulation of media and reactor designing for cost effectiveness and simplification of the process.

Modification of the process to minimise environmental pollution.

The biological aspects include:

- Increasing the rate of metal extraction and
- Enhancing the tolerance of the microorganisms to heavy metals.

In this context, it is necessary to investigate the amenability and detailed behaviour of bioextraction profile for GMDC polymetallic concentrate. This study will help to utilise the national reserves of the mineral resources, which are not exploited due to lack of technology. It also provides some economical benefit by recovering metal values from the polymetallic concentrates, which are not amenable to conventional processes due to obvious reasons.

With above aspects in mind, the present research program was undertaken to optimise and scale-up the bioleaching process for metal extraction from GMDC (Gujarat Mineral Development Corporation) polymetallic concentrate. The research work was designed stepwise as follows:

1. Bioextraction study with various isolated cultures of *Thiobacillus* spp. in pure and mixed forms, selection and development of consortium of iron and sulphur oxidising bacteria.

2. Optimisation of flask scale technique with respect to both biotic and abiotic factors for
   (a) Batch leaching
   (b) Semi-continuous leaching

3. Air-lift Tank leaching

4. 5 dm³ Stirred Tank Reactor (STR) for
   (a) Batch leaching
   (b) Semi-continuous leaching

5. Scale up of the process up to 200 dm³ Bioreactor.