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Bilingual Course of Biohydrometallurgy for Nonferrous Metals

有色金属生物冶金

薛济来　主编

冶金工业出版社
Metallurgical Industry Press

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内 容 提 要

有色金属生物冶金主要采用生物技术来对矿物中的有色金属进行富集、分离、提取和回收利用，通常由微生物来进行矿石的细菌氧化或生物氧化。生物冶金工艺成本低、污染少、资源利用率高，目前已应用于难处理金矿、铜硫化矿等。生物冶金具有超过常规处理贫矿的技术优势，正发展成为国际上有色冶金研究的热点之一。

本书主要内容包括：有色金属生物冶金技术基础、冶金方法、工艺特征和工业应用（提取金、铜、镍、锌）。文中均加以简要注释，以方便自学。书后附相关专业词汇。

本书适用于有色冶金、冶金工程、工业生态、矿物工程、环境工程等专业的高年级本科生和研究生科研和双语教学，也可供研发人员和生产技术人员参考。

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前　言

有色金属在国民经济和国防事业中占有重要的战略地位，是实现工业化、城镇化和信息化的基础支撑材料。当前我国有色金属产业快速发展，同时又面临着资源短缺、环境污染等瓶颈问题。利用生物技术处理低品位矿物和开发环境友好的有色金属提取工艺，是近年来国际上兴起和迅速发展的前沿技术。通过英文文献载体，可直接交流、快捷获取国际上有关这一领域的发展趋势和技术动态的最新信息，有助于从事相关领域的研究开发和专业教育工作。

有色金属生物冶金主要涉及利用细菌和生物技术对矿物和废弃物中所含有色金属进行富集、分离、提取和回收利用。本书内容包括：生物冶金物理化学基础、有色金属生物冶金方法、工业应用（提取铜、金、钴、镍、锌等有色金属）及二次资源综合利用。书中内容主要参考国外有关英文专著和学术期刊，力求保持其英文原貌，并加以简要注释，以方便自修。

本书选编时着重对有关基本原理、方法、典型技术应用的精要介绍，同时兼顾基础性和应用性，可广泛适用于冶金工程、有色冶金、化工、材料、矿物加工、环境和资源工程、生物技术、应用化学等专业的大学高年级本科生、研究生、中高层研发人员和管理人员提升专业知识和当代科技英语水平两方面的需求。

作者多年在北京科技大学冶金与生态工程学院讲授有色金属生物冶金英中双语课程，曾使用过本书内容并在教学过程中获益匪浅。李想、冯鲁兴、张亚楠在本书编辑过程中付出了辛勤劳动，在此一并感谢。

作者深感水平有限，研究不足，书中难免遗漏不当之处，敬希业内同仁和读者指正。

薛济来

2012年8月于北京

Preface

Nonferrous metals play a strategic important role in national economics and defense, which are basic materials supporting developments of industrialization, urbanization and informationization in China for today. The Chinese nonferrous metals industry has made great progress in recent years, while at the same time it faces challenges in resource shortage and environmental pollution. Biotechnology treating low-grade metals ores and creating environment-friendly process to extract nonferrous metals are the internationally emerging and fast developing cut-edge technology. Through English technical literature, you can obtain the most-updated knowledge about the international trend of development in your interesting fields and improve your professional skills and research work.

Biohydrometallurgy for nonferrous metals is dealt with the extracting, concentrating, separating and recycling of nonferrous metals from minerals and spend residues using bacteria and biotechnology. This book contains fundamentals in biotechnology and bacteria, biohydrometallugical processing methods for nonferrous metals, their industrial implementations (extraction of Cu, Au, Co, Ni and Zn metals) and metals recovery from secondary sources. These contents have been referred to scientific books and professional journals in English origin, along with providing explanation notes to assist readers for self-study.

In preparing this book, emphases have been placed on supplying information on fundamentals, processing methods and some typical industrial applications in biohydrometallurgy for nonferrous metals, where a balance is properly made between the technical theory and the industrial reality. The book is intended for senior students, postgraduates and young and middle age professionals in many different fields, such as metallurgical engineering, nonferrous metallurgy, chemical engineering, materials

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technology, minerals engineering, environmental and resource engineering, biotechnology, applied chemistry, etc. It may serve the purpose of improving both their scientific knowledge and contemporary English skill.

The author has used the same contents as mentioned above for several years in teaching bilingual course at School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, and benefited the most from a good interaction between the learning and the teaching during that time. Last but not the least, the author would like to thank Li Xiang, Feng Luxing, and Zhang Yanan for their assistance in preparing this manuscript, and also invite the readers and colleagues to provide their comments and criticism on this edition.

Xue Jilai

Beijing, August 2012

Content

1 Biohydrometallurgy and Bacteria

本章要点 本章简要介绍了生物冶金技术近年来的研究和发展。对微生物、不同温度范围的细菌种类、细菌营养、矿物浸出过程、生物浸出过程、生物冶金技术在有色金属提取冶金中应用的有关概念、技术背景和国内外产业化实例做了概述。

1.1 Introduction

Natural bioleaching has been taking place for almost as long as the history of the world, but it is only in the last few decades that we have realized that bioleaching is responsible for acid production in some mining wastes, and that this bacterial activity can be used to liberate some metals. Today large-scale, biohydrometallurgy facilities extract copper and enhance gold recovery from ores and concentrates, and the commercially applied environmental biotechnologies remediate metal-contaminated waters and degrade cyanide. These commercial operations demonstrate the qualities robust nature, operational simplicity, health, safety and environmental benefits, capital and operating cost advantages and improved performance that have made bioleaching/biooxidation and bioremediation viable process options for the mining and nonferrous metals industry. With commercial success, the industry now anticipates better efficiency from existing biotechnical processes, improvements in applications and novel processes to further enhance the utility and extent of application.

The low pH, metal-rich, inorganic mineral environment in which bioleaching reactions occur is populated by a group of bacteria which are highly adapted to growth under these conditions. The bacteria most commonly isolated from inorganic mining environments are *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans* and *Leptospirillum ferrooxidans*. These bacteria are considered to be the most important in most industrial leaching processes. The recently described moderately thermophilic bacterium, *Thiobacillus caldus*, which grows optimally at 45°C also grows well at between 30°C and 40°C and may be readily isolated from bioleaching processes which operate at this temperature. From a physiological viewpoint this bacterium is the moderately thermophilic equivalent of *Thiobacillus thiooxidans* and the role of *T. caldus* in many industrial operations is almost certainly greater than that has been generally recognized. A number of species of heterotrophs which grow in very close association with the obligate autotrophs have been found, most of which belong to the genus *Acidiphilium*. Other acidophilic bacteria which have been reported from leaching environments include the facultative heterotrophic bacteria *Thiobacillus acidophilus* and *Thiobacillus coprinus*.

This chapter presents a brief description of development in biohydrometallurgy, some fundamentals knowledge about bacteria, nutrition and energy sources, and the extent and scale of commercial biotech-

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nology applications in processing minerals containing nonferrous metals.

1.2 Development in Hydrometallurgy

Although the terms bioleaching and biooxidation are often used interchangeably, there are distinct technical differences between these process technologies. Bioleaching refers to the use of bacteria, principally *Thiobacillus ferrooxidans*, *Leptospirillum ferrooxidans* and thermophilic species of *Sulfobacillus*, *Acidianus* and *Sulfolobus*, to leach a metal of value such as copper, zinc, uranium, nickel and cobalt from a sulfide mineral. Bioleaching places the metal values of interest in the solution phase during oxidation. These solutions are handled for maximum metal recovery and the solid residue is discarded.[1] Minerals biooxidation refers to a pretreatment process that uses the same bacteria as bioleaching to catalyze the degradation of mineral sulfides,[2] usually pyrite or arsenopyrite, which host or occlude gold, silver or both. Biooxidation leaves the metal values in the solid phase and the solution is discarded.

The discovery in 1947 that bacteria are associated with acid rock drainage and the characterization and naming of *Thiobacillus ferrooxidans* in 1951 spurred research on the role of these organisms in oxidizing mineral sulfides. Research published in the 1950s led to the 1958 patent that preceded the industrial scale application of copper dump leaching by Kennecott Copper Corporation in the early 1960s. Research and development between 1960 and 1980 yielded important information:

(1) Metabolic pathways for sulfur and iron oxidation in thiobacilli were described;

(2) Morphological and structural characteristics of the leaching bacteria identified;

(3) Genetics of metal-microbe interactions introduced;

(4) Moderate and extreme thermophiles that oxidize reduced sulfur and iron compounds and mineral sulfides discovered and partially characterized;

(5) Microbial-mineral interactions and mineral metabolism described;

(6) Metal, iron concentration, nutrient, light, pressure, aeration, and temperature, affects on bioleaching quantified;

(7) Extent of microbial leaching of mineral sulfide ores and concentrates (for example, pyrite in coal, arsenic sulfides, chalcopyrite, and complex mineral sulfides) defined;

(8) Ecology of copper dump leach operations studied;

(9) Heterotrophic microbial processes of mineral's leaching surveyed;

(10) Bioleaching of mineral sulfide concentrates in continuous, stirred-tank reactors perfected;

(11) Large-scale test facilities to evaluate copper bioleaching employed.

The results of these studies were chronicled in the International Biohydrometallurgy Symposia of the 1970s, an excellent book on thermophilic microorganisms, and hundreds of journal publications.

The 1990s has been the decade of commercial awakening of bioleaching/biooxidation. Twelve of the world's fourteen commercially-operating facilities were commissioned in the first five years of this decade. This commercial activity sparked notable findings reported in an increasing number of journal publications and symposia devoted to the discipline. Research and development were made in the biochemistry, genetics and molecular aspects of the leaching organisms and-at the other end of the spectrum-test work requirements, engineering considerations and economics of tank and heap bioleaching/biooxidation scale-up. It is somehow paradoxical that, despite the considerable advances that have been made over these years, a fundamental aspect-the relative importance and contribution of direct and indirect leaching-eludes scientists and practitioners of the technology.

Commercial applications of aerated, stirred tanks for refractory-sulfidic gold concentrates and bioheaps for chalcocite and refractory-sulfidic gold ores have shifted the focus of R&D somewhat to topics that will improve these processes, diminish capital and operating costs and extend the process applications. Achievements made in this context are:

(1) Improved aeration systems for stirred-tanks that will improve utilization efficiency, and decrease operating costs;

(2) Aerated, stirred-tank and bacterial ferric generation systems for chalcopyrite concentrate bioleaching developments that promise significant cost reductions over smelting and could open new mines in remote locations;

(3) Aerated, stirred tanks for Co, Zn and other mineral sulfide bioleaching and for recovery of less-common metals (e.g., In);

(4) Bioheap leaching of concentrates, which would reduce capital and operating costs for processing concentrates;

(5) Techniques to decrease cyanide consumption of biooxidized residues, reducing operating costs of gold plants;

(6) Innovative bioheap technologies for diverse climates (e.g., high rainfall areas, tropics, Arctic regions), disparate ore types (e.g., clayey ores), and enhanced aeration;

(7) Effective application of extremely thermophilic bacteria in stirred-tank reactors and bioheaps;

(8) Better understanding of solution chemistry equilibria in bioheaps to improve kinetics and minimize leach solution treatment costs.

Biooxidation/bioleaching research that promises to make a difference from a fundamentals perspective encompasses:

(1) Bioleaching of chalcopyrite ore to allow low-cost heap and in situ leaching of deposits;

(2) Genetically altered bacteria which improve biooxidation/bioleaching and can electively compete with native bacteria in commercial plants;

(3) Definitive understanding of the direct versus indirect attack and the relative importance to stirred tank and bioheap reactors.

In China, the biohydrometallurgy has been also developed in recent years and has been applied to a large extent in industrial productions. Zijinshan Gold & Copper Mine is situated 14.6km north of Shanghang county in Fujian province, along the left band of the beautiful and picturesque Tingjiang river (Fig. 1.1). It has extremely rich gold and copper reserves. According to historical records, people have panned for gold here since the Sung Dynasty (around 1040 AD). Zijinshan Mine is one of the large non-ferrous metal mines being discovered in the 1980s in China. It has a typical vertical zoning with gold in the upper zone and copper underneath, which is a super-large scale porphyry-type ore deposits. Gold deposited at 600-1100m elevation within the oxidation zone, while copper sulfide ores below the 600-700m elevation. Zijinshan Gold & Copper Mine has been to be a large scale successful example of gold heap leaching in this humid and rainy environment in southern China. Furthermore, Zijinshan copper mine is the largest chalcocite deposit in China. The attempt to recover copper from the ore by bioleaching began at the end of 1998. Following the metallurgical studies carried out over 2 years, a pilot plant consisting of bio-heap leaching and SX–EW was built at the Zijinshan copper mine at the end of 2000, with a production capacity of 300t/a copper cathode. After its successful operation for 1.5 years, the plant was scaled up to a capacity of 1,000t/a copper cathode by june 2002. In 2005, a commercial bio-heap leach plant with a capacity of 10,000t/a was built.

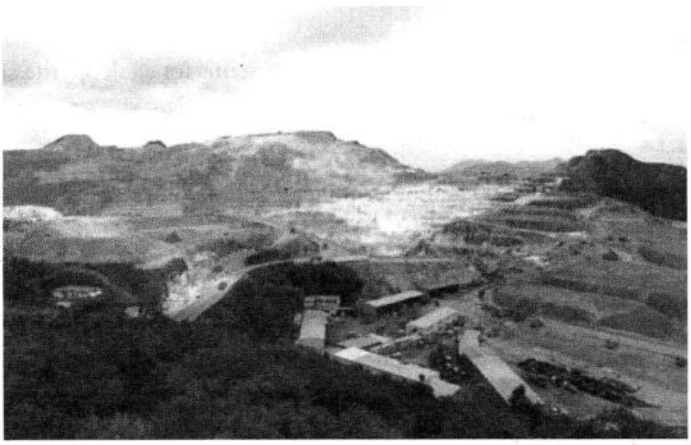


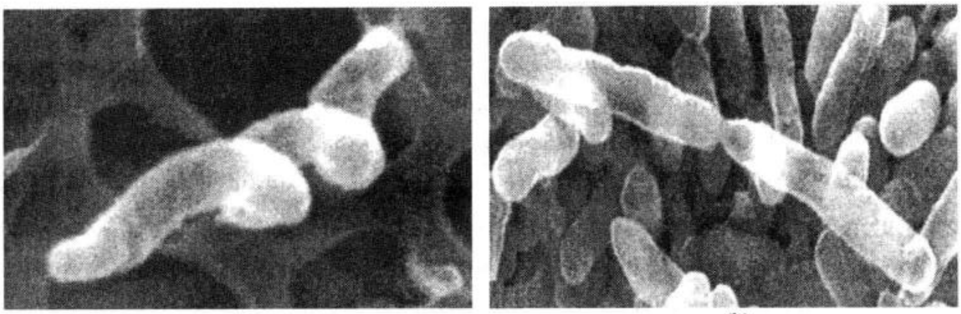
Fig. 1.1 Zijin opencaste gold mining

In order to improve research and technology in biohydrometallurgy in China, two state key laboratories have been built in recent years. One is the Key Laboratory of Biometallurgy of Ministry of Education in Central South University and another is National Engineering Laboratory of Biometallurgy supported by General Research Institute for Nonferrous Metals.

1.3 Bacteria and Phylogeny

T. ferrooxidans, *T. thiooxidans* and *L. ferroxidans* are used in bioleaching process, which are all autotrophic and acidophilic bacteria. Both *T. ferrooxidans* and *T. thiooxidans* are rod-shaped while *L. ferrooxidans* is spiral-shape, as shown in Fig. 1.2. *T. ferrooxidans* is able to use ferrous iron or reduced sulfur compounds as an electron donor, while *T. thiooxidans* is capable of using only reduced sulfur compounds and *L. ferrooxidans*, only ferrous iron. All three bacteria use oxygen as a terminal electron acceptor, although *T. ferrooxidans* is able to grow using ferric iron as an electron acceptor provided reduced sulfur compounds are available to serve as an electron donor.

T. ferrooxidans has been described as a species of convenience. Based upon DNA IA homology studies, strains called *T. ferrooxidans* were placed by Harrison into as many as seven subgroups. Five *T. ferrooxidans* homology subgroups had G+C contents of 56%-59%, one subgroup was shown to be an *L. ferrooxidans* isolate and another, represented by a single isolate (*T. ferrooxidans* m-1) had a G+C content of 65% and has not been shown to oxidize sulfur. Therefore only five of the subgroups can be considered to be *T. ferrooxidans*.



(a) (b)

Fig. 1.2 A scanning electron microscope image of (a) *L. ferrooxidans* DSM2705 (×18000) and (b) *T. ferrooxidans* ATCC33020 (×15000)

T. thiooxidans may also consist of more than one grouping with most strains having a G+C content of 52%-53%. An exception is strain DSM612 which has a 62% G+C content and may be more similar to *Thiobacillus albertis*. Another strain has a G+C content of 58%, which falls within the range for *T. ferrooxidans*. A difficulty in using the ability to oxidize iron or sulfur as a means of distinguishing *T. ferrooxidans* from *T. thiooxidans* is that many *T. ferrooxidans* strains may exhibit a delay in switching between iron with the result that researchers may assume that the organism is incapable of oxidizing one or other energy source.

The taxonomic status of the genus *Leptospirillum* remains to be fully resolved. There is no valid description of the organism in Bergey's Manual of Determinative Bacteriology, although reference is made to *Leptospirillum* in the section on the genus *Thiobacillus*. *Acidiophilic*, obligate autotrophic bacteria which grow on ferrous iron and sulfide minerals and which have a helically curved rod-shaped morphology are considered to be strains of *Leptospirillum*. The spiral forms can be of varying length and generally have a long polar flagellum. The bacterium was originally described by Markosyan from samples collected in Armenia but there is evidence that this *L. ferrooxidans* L15 strain may be atypical. Harrison and Norris compared protein electrophoretic patterns, DNA-DNA homology and mol% G+C ratios for *L. ferrooxidans* and several *Leptospirillum*-like bacteria. They found that the bacteria could be divided into two groups with a G+C content of either 51%-52% or 55%-56mol%. Bacteria which fit the description of *L. ferrooxidans* have been isolated from numerous environments including water samples from uranium mines in Canada and Mexico, copper mines in the USA, a mine in Bulgaria, coil spoil heaps in England, mine samples in Australia and biooxidation plants in South Africa. *L. ferrooxidans* is as ubiquitous as *T. ferrooxidans* and *T. thiooxidans*.

The important leaching organisms grow in acidic, inorganic habitats and in many instances cannot tolerate more than traces of organic matter.❸ These bacteria could therefore be expected to have evolved in relative isolation from other bacteria. Prior to the advent of DNA and RNA sequencing techniques it was not possible to determine the evolutionary relationship of the acidophilic autotrophs to the rest of the bacterial kingdom. A considerable amount of molecular sequence information has become available within the past 10 years including partial and complete 5S rRNA and 16S rRNA sequences. Based on these sequences *T. ferrooxidans* and *T. thiooxidans* isolates are closely related and have been placed within the proteobacteria at a point close to the division between the β and γ subgroups.

The sequences of a number of other molecules such as the genes for the RecA protein, glutamine synthesizes and the β subunit of the F_1F_0 ATP synthase have been determined from a large number of bacteria. Phylogeny based on the amino acid sequences of the RecA protein, glutamine synthetase and the β subunit of the F_1F_0 ATP synthase have confirmed the classification of *T. ferrooxidans* as a β proteobacterium. An interesting exception is the product of the *nifH* gene. The *T. ferrooxidans* nitrogenase iron protein is clearly most closely related to the equivalent proteins of the genus *Bradyrhizobium*, which is an x proteobacterium, and may be an example of lateral gene transfer.

Lane et al., analyzed partial 16S rRNA sequences of three isolates of *Leptospirillum*-like bacteria. They reported that although the three isolates were closely related to each other (ca. 94% similar), they were not specifically related to any of the existing divisions of bacteria and suggested that the leptospspirilli may represent a new phylogenetic division. Near complete 16S rRNA sequence data of represent a new phylogenetic division. Near complete 16S rRNA sequence data of in the construction of Fig. 1.3. There is a discrepancy in the relationship of the genus *Leptospirillum* to other bacteria if one compares the information in the Ribosome Database Project (WWW) with that in the National Center for Biotech-

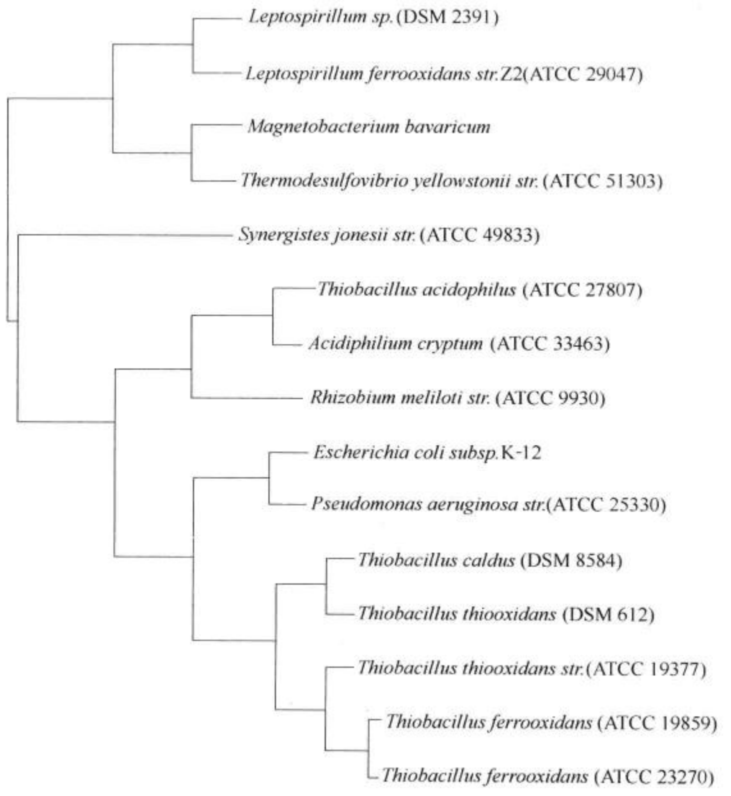


Fig. 1.3 Dendrogram showing the phylogenetic relationship between the relatively closely related bacteria *T. ferrooxidans*, *T. thiooxidans* and *T. caldus* and the distantly related *Leptospirillum* species

(The dendrogram was constructed based on 16S rRNA sequences using the Ribosome Database Project website (http://www.rdp.life.uiuc.edu)) nology Information (NCBI) taxonomy base (WWW). In the NCBI data base the leptospirilli have been placed within the group *Nitrospira* whereas the managers of the Ribosome Database Project have not recognized a *Nitrospira* group. It is interesting that one of the closest bacterial relatives to members of the genus *Leptospirillum* that has been reported so far is the magnetotactic bacterium *Magnetobacterium bavaricum*.

1.4 Nutrition

Bacteria in bioleaching have very modest nutritional requirements. Aeration of a sample of iron pyrite in acidified water is sufficient to support the growth of *T. ferrooxicians* and *L. ferrooxidans*.[4] Air provides the carbon, nitrogen and oxygen source, pyrite the energy source and trace elements, and acidified water the growth environment. *T. thiooxidans* is not able to oxidize ferrous iron to produce the ferric iron required to attack the mineral, however, it readily grows on pyrite in combination with either *T. ferrooxidans* or *L. ferrooxidans*.

1.4.1 Carbon nutrition sources

T. ferrooxidans strains that have been confirmed as being pure are obligate autotrophs. Some early studies showed that after a period of adaptation *T. ferrooxidans* was able to grow on organic substrates and that this was followed by a permanent loss of the ability to oxidize iron. However, the G+C mol% ratio of the cultures changed under these conditions and heterotrophic growth was almost certainly due to the inability of researchers to free their cultures from the presence of the closely associated heterotrophic bacteria belonging to the genus *Acidiphilium*. The iron-dependent, mixotrophic growth of one strain has been reported but unfortunately that isolate has been lost.

Carbon dioxide fixation in *T. ferrooxidans* takes place via the Calvin reductive pentose phosphate cycle. One of the most important enzymes in this process, ribulose 1, 5-biphosphate carboxylase (RuBPCase) has been characterized. This work also showed that growth on ferrous iron was reduced unless the concentration of CO_2 in the air was increased. This observation is in contrast to the work of others in which it was found that the concentration of CO_2 in air was sufficient to avoid limitation on growth on ferrous iron and mineral sulfide oxidation by *T. ferrooxidans*. The bacterium responds to CO_2 limitation by increasing the cellular concentration of RuBPCase. Indeed, *T. ferrooxidans* strain Fe_1 has two sets of the structural genes for RuBPCase. The two sets are separated by more than 5kb and the nucleotide sequence of the coding region of each set is identical although the flanking regions varied substantially. The RuBPCase gene regulator, RbcR, has been isolated and sequenced. Very little work has been carried out on the enzymology or genetics of CO_2 fixation by either *L. ferrooxidans* or *T. thiooxidans*.

1.4.2 Nitrogen nutrition sources

The study of the nitrogen requirements of bioleaching organisms is complied by the phenomenon that ammonia is highly soluble in acid solutions. Atmospheric ammonia readily dissolves in leach solutions and may provide most, if not all, of the nitrogen required for growth. As little as 0.2mmol/L ammonium has been reported to be sufficient to satisfy the nitrogen requirement of *T. ferrooxidans*. This value will be dependent on the amount of ferrous iron or mineral present in the medium or leach liquor.

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