BACTERIAL LEACHING OF COPPER FROM LOW GRADE CHALCOPYRITE ORES

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ABSTRACT

A brief account is given of the observations on the occurrence of the species of Thiobacillus *in the shaft water near the mines at Ingaldhal (Karnataka State), its isolation, cultivation and utilization, on a laboratory scale, in leaching out copper from low grade chalcopyrite ore. In the experiment conducted, from* 40 *lbs of the ore containing* 0·6 *per cent copper,* 18 *grams of copper (Cu) was obtained. These and other observations indicate the possible utilization of this and similar organisms in the commercial production of copper from low grade chalcopyrite ores occurring in large quantities in Karnataka State and elsewhere.*

Keywords: Bacterial leaching, chalcopyrite ore, copper.

INTRODUCTION

IN certain parts of the world large quantities of low grade chalcopyrite ores containing 0·2 to 0·8 per cent copper occur. The customary chemical and other methods of extraction of copper from such ores are not economical, and therefore attempts are seldom made to extract the copper in these ores. At the same time the possibility of utilizing the activities of certain microorganisms occurring in the copper mining areas has been studied to some extent.

As early as 1670 copper was being recovered from mine drainage waters at Rio Tinto operations in south-western Spain, but at that time the existence of microorganisms was not known and so there was no idea of microbial activity on chalcopyrite ore to bring the copper into solution [1]. Around that time, however, microscope was being invented and Leeuwenhoek was indeed the first to see microorganisms under a variety of conditions in Nature. But techniques and methods were lacking to demonstrate the microbial activity. These were gradually developed in the latter half of the last century and great advances were made in the science of microbiology.

In 1904 Beijerinck isolated and studied an organism which he designated *Thiobacillus denitrificans*. This organism occurs as minute, motile rods. When it is grown under aerobic conditions, it oxidizes sulphur and thiosulphate to sulphuric acid without forming sulphur deposits [2]. The activities of this and similar organisms in the sulphur cycle, which are closely connected with the release of other elements and metals from other sulphide ores under natural conditions, were however not related to the formation of large quantities of copper when water was passed through chalcopyrite-pyrite heaps during Rio Tinto operations in Spain in the first half of this century [1].

This empirical practice of leaching of ore dumps continued for many years on a commercial scale in Peru, the western United States, Canada, Africa, and in other places until 1947 when Colmer and his associates [3, 4] isolated from the acidic drainage waters of a West Virginia coal mine *Thiobacillus ferrooxidans* which is involved in the oxidation of ferrous to ferric sulphate. Since then attempts have been made in certain parts of the world to utilize the activities of the species of *Thiobacillus* for the recovery of copper and other metals from ores in which the concentrations of these metals are too low for commercial production by the usual chemical and other methods [2–10].

In discussing the recent developments, particularly on the role of bacteria in copper mining operations [9], it was pointed out that "our understanding of the role of microorganisms in leaching of sulphide ores under field conditions may, at best, be described as incomplete" and that while "laboratory studies show microbial activity to be the major cause of rapid solubilization of copper sulfide ores, field studies suggest that microbial activity cannot explain all observations in a typical leaching operation". Investigations on water and waste water have been proceeding in this laboratory for over 50 years [11], and in the course of an inquiry into the highly acidic (pH 2·3) water from a shaft near a copper mine at Ingaldhal, Karnataka State, led to the present study of bacterial leaching of copper from low grade chalcopyrite ores.

MATERIALS AND METHODS

In the company of Dr. B. P. Radhakrishna, the then Director, Department of Mines and Geology, Government of Karnataka, we visited Ingaldhal, where a considerable quantity of low grade copper ore occurs, and collected samples of water from a shaft near a copper mine, samples of other waters in that area and samples of the ore for analysis. The ore was broken in a mortar down to about ½ inch size for the experiment.

The water samples were analysed for turbidity and pH. The shaft water was analyzed also for total solids, copper, iron, sulphur, magnesium, and calcium. The ore samples were analysed for copper and iron.

The turbidity was measured by determining the light transmission in a Klett-Summerson photoelectric colorimeter using a blue filter (maximum transmission at 420 mμ). The pH was measured using Elico pH meter with glass electrodes. Copper was estimated by the volumetric analysis after adding fluoride to suppress the activity of iron and titrating the liberated iodine from potassium iodide against sodium thiosulphate, iron by stannous chloride reduction and sulphur by barium sulphate method [12]. Calcium and magnesium were determined by the EDTA titration method using Eriochrome Black T [13].

EXPERIMENTAL

Analysis of the Water from the Shaft near the Copper Mine

The results of analysis of the different samples of water from the same area at Ingaldhal are given in Table I. The water from the bore-well near the guest house on the campus (the water from this well is used for drinking) had a pH value of 7·5. The rain water which was stagnating in a shallow pit near the mining area had a pH value of 9·5 (we visited the mining area in May 1970 and the rainfall during that month was about 67 mm). It

TABLE I

Results of analysis of water from Ingaldhal

Water sample	Turbidity	pH
1. Stagnant water from a shaft in the mining area*	100	2·3
2. Rain water standing in a shallow pit near the shaft**	130	9·5
3. Bore-well water near the guest house	Nil	7·5
4. Tap water from the laboratory	4	7·1

* This water was reddish-brown in colour.

** This water was reddish in colour.

was of considerable interest to note that the pH value of the shaft water was 2·3; that it contained *Thiobacillus* sp. which can tolerate a low pH; and that it contained 8·234 gm solids (dry weight) per litre, with a high percentage of sulphur (sulphate) but that it did not show any copper. The solids contained, as percentage on dry weight basis: sulphur (S, including SO_4^{2-}), 22·41; iron (Fe), 7·49; magnesium (Mg), 7·71; and calcium (Ca), 6·41. This analysis was carried out with the kind assistance of Prof. C. C. Patel of the Department of Inorganic and Physical Chemistry at this Institute.

Observations on Thiobacillus *Sp. Isolated from the Mine Water*

This organism was cultivated in a liquid medium, the composition of which is given in Table II. During the growth of this organism over a period of 10 days, the pH of the medium decreased to 2·3 (Fig. 1).

This organism was used for leaching out the copper from low grade chalcopyrite ore which contained 0·6 per cent copper. The copper contents of the samples of low grade chalcopyrite ore ranged from 0·2 to 0·8 per cent. Sporadic deposits of higher grade copper ores also occur at Ingaldhal; the copper contents of such ores ranged from 1·8 to 8 per cent.

TABLE II

The composition of the medium used for the cultivation of Thiobacillus *sp.*

Constituent	Amount
Ferrous sulphate, $FeSO_4 . 7H_2O$	10·00 gm
Ammonium sulphate, $(NH_4)_2 SO_4$	3·00 gm
Potassium chloride, KCl	0·10 gm
Potassium monohydrogen phosphate, $K_2HPO_4 . 3H_2O$	0·50 gm
Ma gneum sulphate, $MgSO_4 . 7H_2O$	0·50 gm
Calcium nitrate, $Ca (NO_3)_2$	0·01 gm
Sulphuric acid (10 N)	1·0 ml
Distilled water	1000 ml

The pH of this medium is 3·2.

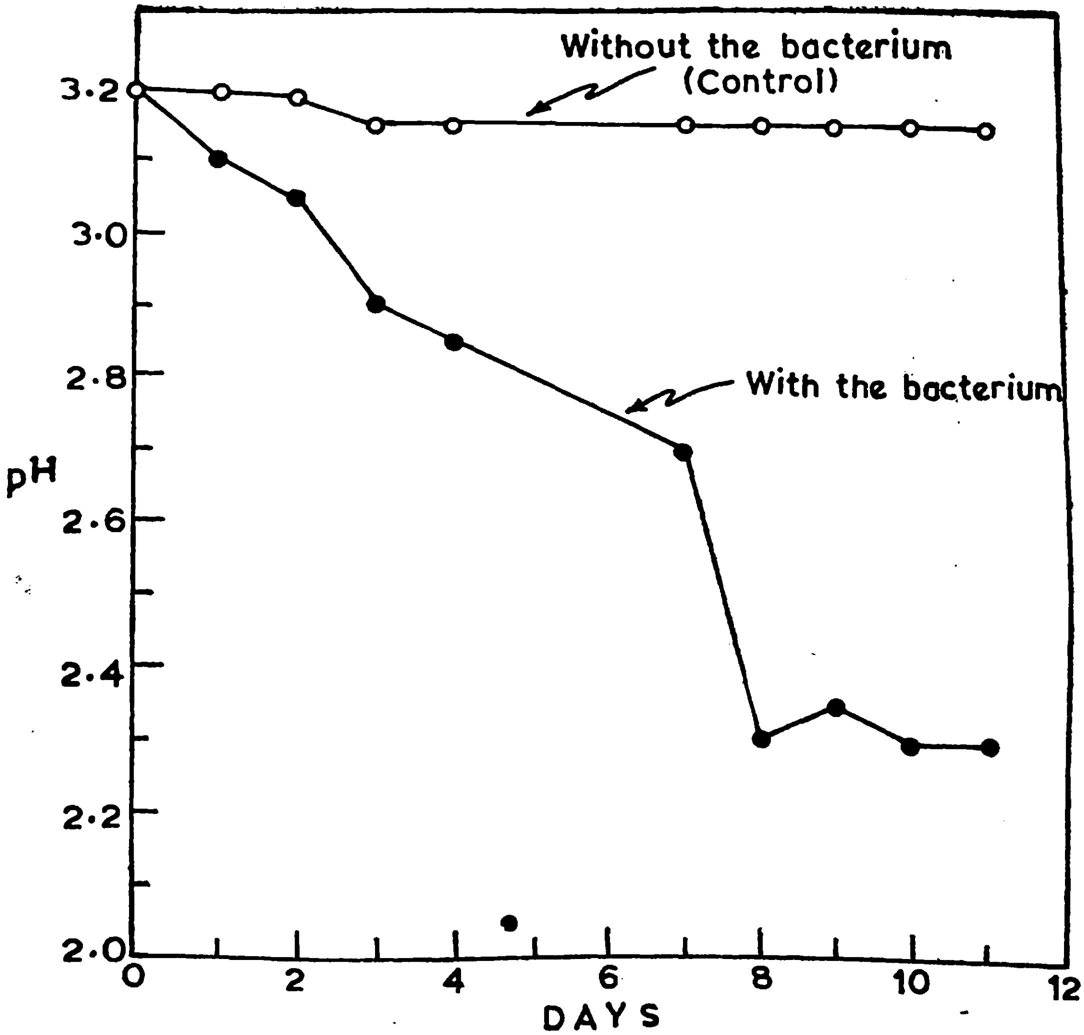

FIG. 1. Effect of the growth of *Thiobacillus* sp. on the pH of the meaium.

Treatment of Low Grade Chalocopyrite Ore and Extraction of Copper

40 lbs of the crushed ore (½ inch size) was taken in a glazed pot (34 cm depth and 26·5 cm diameter, with provision for drainage; Fig. 2) and the material was inoculated with 100 ml of 15-day old culture of *Thiobacillus* sp., together with 3 litres of leach liquor which contained all the ingredients of the bacterial culture medium except ferrous sulphate (Table II). Ferrous sulphate was eliminated from this medium because the ore provides sufficient amount of this ingredient. The pH of the leach liquor was adjusted to 5. There was a control glazed pot with the ore and leach liquor but without the organism.

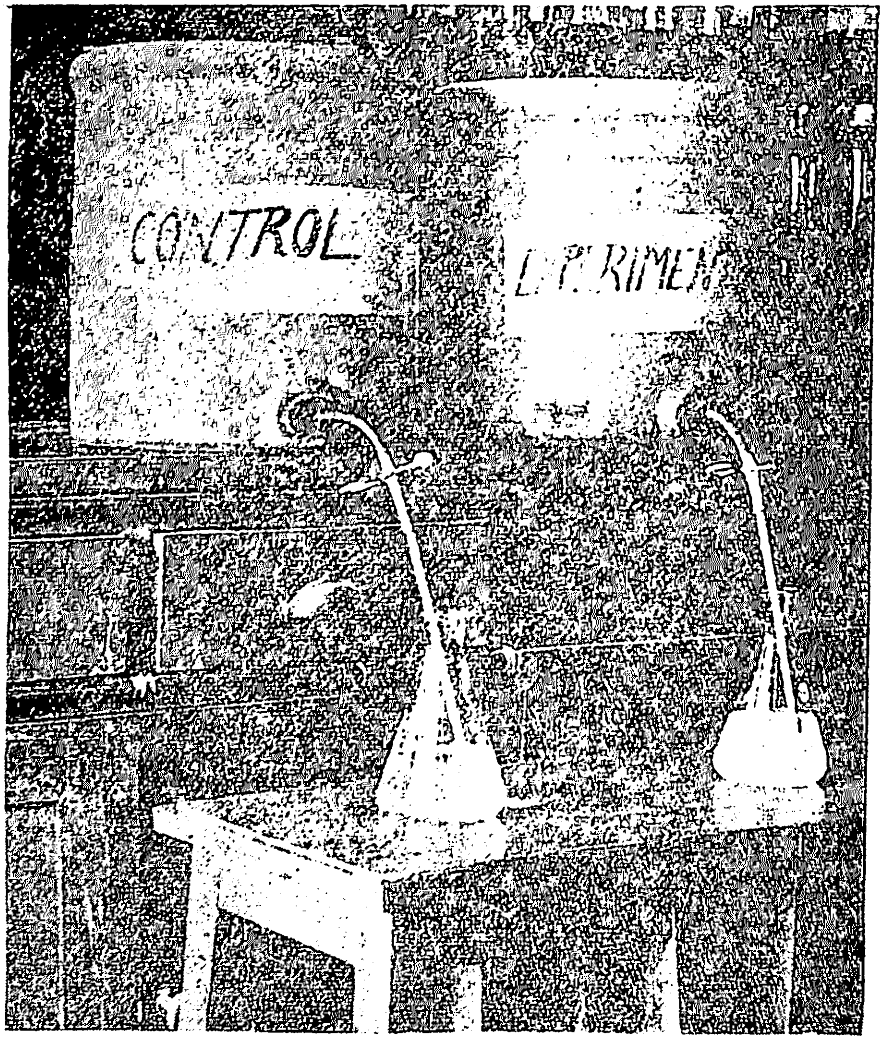

FIG. 2. The glazed pots in which the crushed chalcopyrite ore was taken for leaching out the copper.

The leach liquor was allowed to trickle through the ore chips at the rate of 3 litres per hour and the liquid drained was poured back and this process of recirculation was repeated 6 times a day. When the concentration of copper reached 250 mg Cu per litre, the leaching appeared to be retarded. When the copper concentration in the liquor was lowered by 'cementing out' copper with iron filings, leaching proceeded as indicated by steady increase in the copper content of the leach liquor.

The ore, which was acted upon by the bacteria, lost the bright brassy shine and became dull and grey. The leach liquors also showed charac-

TABLE III

Results of the laboratory trial in leaching out copper from a sample of chalcopyrite ore available at Ingladhal

The amount of the ore taken	40 lbs
The size of the ore ($CuFeS_2$ containing 0·6 per cent Cu)	½ inch
The volume of the leach liquor (pH 5), *i.e.* the medium without $FeSO_4$, for the growth of the bacterium, *Thiobacillus* sp.	3 litres
The bacterial culture added (15-day old)	100 ml
The total period of recirculation of the bacterial medium (6 times a day) through the ore material	2 months
The amount of copper (Cu) leached out	18gm
Copper extracted from the ore	17%

teristic differences: the liquor from the control pot was clear and pale brown in colour, but the bacterial leach liquor was pale bluish green and turbid. The pH of the liquor in the control pot was 4·8, whereas the pH of the bacterial leach liquor was 2·0.

After two months of leaching, 18 gm of copper was extracted from 40 lbs of the ore. The reddish-brown metal was repeatedly washed (to remove the acid) and dried. The dry powder was compacted and sintered in carbon atmosphere at a temperature of 1000° C (with the kind assistance of Dr. D. B. Ghare in the Department of High Voltage Engineering at this Institute) to obtain pellets of the metal. This yield is about 17 per cent of the copper contained in the ore.

The principle and the chemical reactions involved in the bacterial leaching of copper from low grade chalcopyrite ore and the procedure adopted in the laboratory experiments are indicated in Fig. 3.

Further work is necessary to ascertain the optimum conditions for the maximum extraction of copper from the ore. These conditions include particle size of the ore, pH, temperature, oxygen and carbon dioxide supply, the availability of nutrients for the organism and the external supply

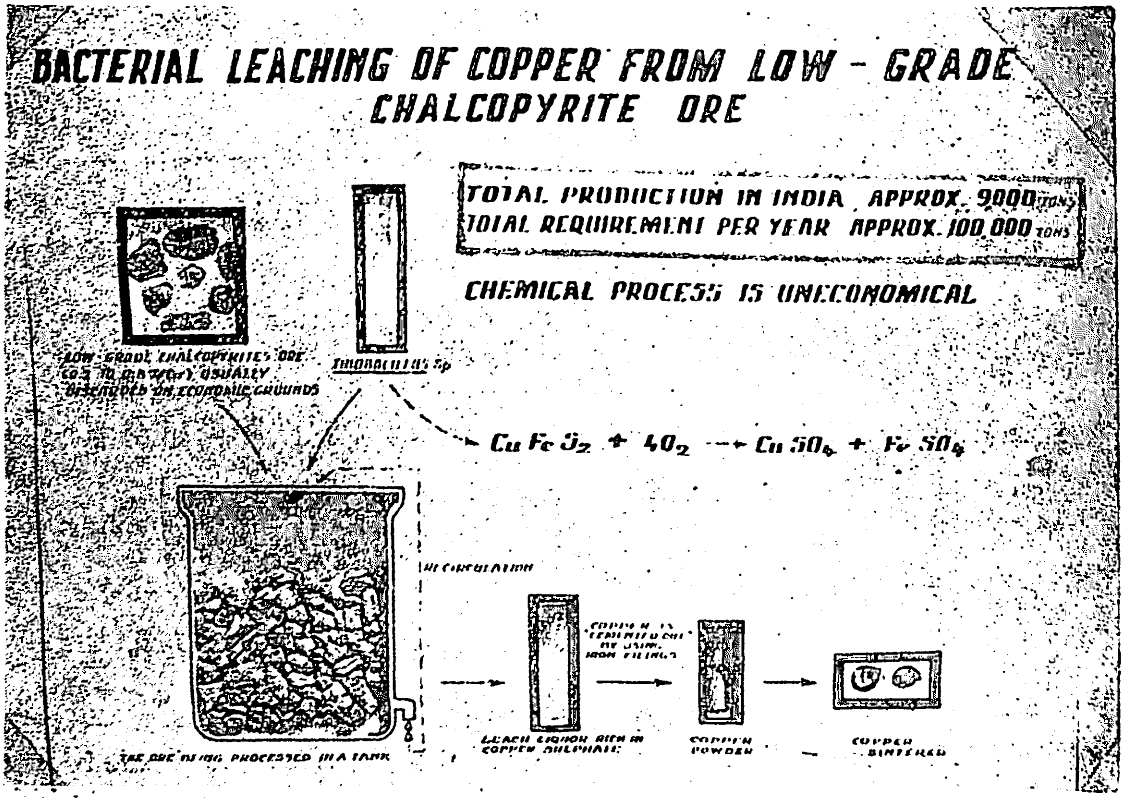

FIG. 3. Showing the crushed ore and the chemical reactions involved in the bacterial leaching of copper.

of ferric iron. The ferric ion is presumed to oxidize the ore and is returned to the active, oxidized state by the iron-oxidizing bacteria [6].

Discussion

The activity of certain microorganisms to leach out copper from chalcopyrite ore is a remarkable process in Nature, which is not only of considerable practical importance but also of great scientific interest. The usefulness of microbial activity here lies in the possible commercial production of copper from low grade chalcopyrite ores (containing 0·2 to 0·8 per cent copper), which cannot be processed economically by other methods. In Karnataka State, in one area alone, the results of preliminary drilling exploration have indicated the existence of reserves up to 10,000,000 tons of a possible grade of 0·7 per cent of copper worked to a depth of 500 feet [14].

Although the observations given in this paper may be regarded as preliminary, they do indicate considerable possibilities in the production of copper not only from the naturally occurring low grade copper ores but also from the tailings from flotation plants. Bacterial leaching may be operated here as a supplementary process.

Another aspect of industrial importance is the possible simultaneous utilization of *Thiobacillus* sp. in the production of sulphur in the process of leaching out copper from the ore containing sulphide, along with iron and other metals, since the organism oxidizes the sulphide to sulphuric acid which brings into solution all these metals. It was reported that "during iron oxidation *T. ferroxidans* was able to tolerate high concentrations of copper, zinc, nickel, cobalt, manganese, and aluminium (more than 10 grams per litre) and that during sulphur oxidation, the tolerance to heavy metals extended to concentrations above 5 grams per litre" [8].

Further studies on the different aspects of these and similar organisms might suggest ways and means of fuller utilization of this biotic force in the production of copper as well as other metals and elements notably sulphur.

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