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Bioleaching of ocean manganese nodules in the presence of reducing agents

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ABSTRACT

The key for successful and efficient dissolution of copper, nickel and cobalt from the ocean manganese nodules depend on prior reduction of manganese and ferric oxides with which the above valuable nonferrous metals are interlocked. The present work is relevant to bioleaching of ocean manganese nodules using autotrophic microorganisms, such as *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* in the presence of pyrite and sucrose which resulted in significant dissolution of copper, nickel and cobalt from the ocean manganese nodules. Electrochemical means of creating reducing conditions in situ are also brought out. Various biochemical and electrochemical mechanisms in the leaching process are outlined.

Keywords: Ocean manganese nodule; Bioleaching; Galvanic couple

1. INTRODUCTION

Biohydrometallurgy has been developed as a discipline and an alternative process for the extraction of metals such as copper, uranium, gold and cobalt and offers many innovative solutions to the hydrometallurgists. But till now bioleaching of ocean manganese nodule has not been commercialized on a pilot or industrial scale in the world. Microbial leaching using chemolithotropic bacteria *Thiobacilli* is a well established phenomena for treating the sulphide minerals and has also been commercially exploited since the last 20 years. Since extensively naturally occurring ocean manganese nodules on the sea floor of all oceans including Indian Ocean are biogenic, there is evidence of presence of mixed population of manganese oxidising and reducing bacteria as well as bacteria which even do not act on manganese of nodule. Many chemical processes based on different approaches have been reported for extraction of the valuable metals from ocean manganese nodules (Kanungo et al., 1988 a, b; Jana et al., 1990 and Han et al., 1975). However, only few investigations have been carried out on the bioleaching of ocean manganese nodules (Yauhiro et al., 1997). It has been found that glycerol, alcohol, mannitol and glucose favored oxidation, acting either as stimulants or playing a part in the structural requirements of the organism (Waksman and Joffe, 1922).

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Biooxidation of sulphur by *Thiobacillus thiooxidans* was not affected in concentration as high as 5 percent of glucose (Waksman and Starkey, 1923).

In this paper a novel, microaerobic, autotrophic microbial leaching system for ocean manganese nodule is described in the presence and absence of reducing agents such as pyrite and sucrose. The hydrometallurgical treatment of ocean manganese nodule has been studied in the presence of sulphur oxidising bacteria, *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* along with sulphur alone as well as with sulphide mineral, pyrite and sucrose to liberate the occluded valuable metals from Mn and Fe lattices. Reductive leaching of ocean manganese nodules in the presence of FeS_2 in H_2SO_4 and microbiologically produced metabolite is primarily accomplished by the action of corrosion couple, MnO_2/Fe^{2+} and galvanic couple.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Ocean manganese nodule samples were collected from the Indian Ocean by National Institute of Oceanography, Goa. The sample was air dried, ground and sieved to obtain the -74 and +53μm fraction. The chemical composition of the ocean manganese nodule sample is given in Table 1. The ocean manganese nodule samples are essentially composite mixtures of oxides/hydroxides of manganese and iron oxides in which oxides of copper, nickel and cobalt are interlocked. X-ray diffraction and mineralogical analysis indicated the presence of todorokite, manganite, birnesite, goethite, maghemite and hematite as the manganese and iron minerals in the ocean manganese nodule sample. Prior reduction of manganic and ferric oxides is therefore a prerequisite to liberate the associated nonferrous metal values before any significant acid dissolution can be achieved.

Table 1
Chemical composition of the ocean manganese nodule sample

Element	%
Mn	24
Fe	10
Ni	1.1
Cu	1.2
Co	0.14

2.2. Microorganisms

Strains of *Thiobacillus thiooxidans* (MCMB 41) and *Thiobacillus ferrooxidans* (TfH6) isolated from Hutti Gold Mines, India were used. The *Thiobacillus thiooxidans* culture was grown in the basal $9K^{-}$ medium, the composition of which is given in Table 2.

The TfH6 strain was well adapted to sulphur medium by serial subculturing in $9K^-$ medium with 10g/l sulphur. To carry out the bioleaching experiments the cell suspension was used. To obtain the cell suspension the culture was filtered through Whatman 42 filter paper to remove the residual S and the filtrate was then centrifuged in Sorvall RC5B refrigerated Centrifuge at 10000rpm using SS34 rotor for 15 minutes. The cell pellet obtained was finally suspended in 100ml of $9K^-$ and used in the experiments.

Table 2
Composition of the basal medium

Medium	g/l
$(NH_4)_2SO_4$	2.0
K_2HPO_4	0.5
$MgSO_4.7H_2O$	0.25
Sulphur powder	10
pH	2.0

2.3. Methods

Chemical leaching and bioleaching experiments in the presence of reducing agents were carried out in 500ml Erlenmeyer flasks using 2% pulp density of –74 and +53µm size fraction of the ocean manganese nodule in the desired media and kept for shaking on a rotary shaker at 160rpm at room temperature. Bioleaching experiments were also carried out in the presence of pyrite at different ratios of nodule:pyrite with metabolite+cells of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* to study the effect of surface area. Bioleaching experiments with *Thiobacillus thiooxidans* and their metabolite have been carried out in the presence of sucrose under similar conditions. Since the bacteria used in leaching were aerobic, appropriate aeration through passage of sterilised air was done in all the bioleaching experiments to provide oxygen and carbon dioxide required for bacterial metabolism. Metabolites used in leaching studies were generated by growth of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* in $9K^-$ and sulphur–rich media for a period of about 60 hours and removing the bacterial cells through centrifugation and filtration. In all leaching experiments a pulp density of 2% was used.

Electrobioleaching experiments were carried out in a three electrode electrochemical cell using –74 and +53µm size fraction of ocean manganese nodule sample at 30°C. It essentially consisted of three pyrex glass compartments of cylindrical cross section having a capacity of 800, 400 and 50ml respectively surrounded by a glass jacket to permit circulation of thermostated water for maintaining constant temperature (30°C).

A platinum mesh electrode submerged into compartment containing the mineral slurry served as the working electrode which was separated by inserting into a fritted pyrex glass of cylindrical cross section in which a platinum foil auxiliary electrode was introduced. The third compartment containing an SCE electrode served as reference electrode, connected through a Luggin capillary.

Before carrying out experiment an agar KCl-bridge was made to prevent the intermixing of slurry with the electrolyte.

The mineral slurry was kept under constant agitation using a magnetic stirrer. Desired potentials were applied using an EG&G model 362 potentiostat and 365 current booster. Ocean manganese nodule samples were characterized before and after leaching through XRD and SEM (EDAX) to reveal the mineralogical phases.

3. RESULTS AND DISCUSSION

Dissolution behavior of the ocean manganese nodule samples in 1M H_2SO_4 in the absence of any added reducing agent is illustrated in Figure 1. After 48 hours of leaching about 60-70% of copper, nickel and iron could be dissolved while cobalt dissolution was only about 18% with negligible manganese in solution. Results from this exploratory leach tests indicate that at least 60% of the nickel, iron and copper present in the nodule are liberated and readily acid soluble. Most of the cobalt (at least 80%) and the rest of nickel and copper (30-40%) are associated with manganese oxides whose reduction and dissolution is a prerequisite for their complete dissolution. The cobalt values are present as Co_2O_3 (higher oxidation state). Prior or simultaneous reduction of manganese and iron oxides holds the key for the liberation and dissolution of associated nonferrous metal values such as copper, nickel and cobalt. Reducing agents such as SO_2, glucose and ferrous sulphate have been used by earlier investigators to enhance leaching of manganiferrous ores in acid media (Khalafalla et al., 1981; Trifoni et al., 2000; Das et al., 1982).

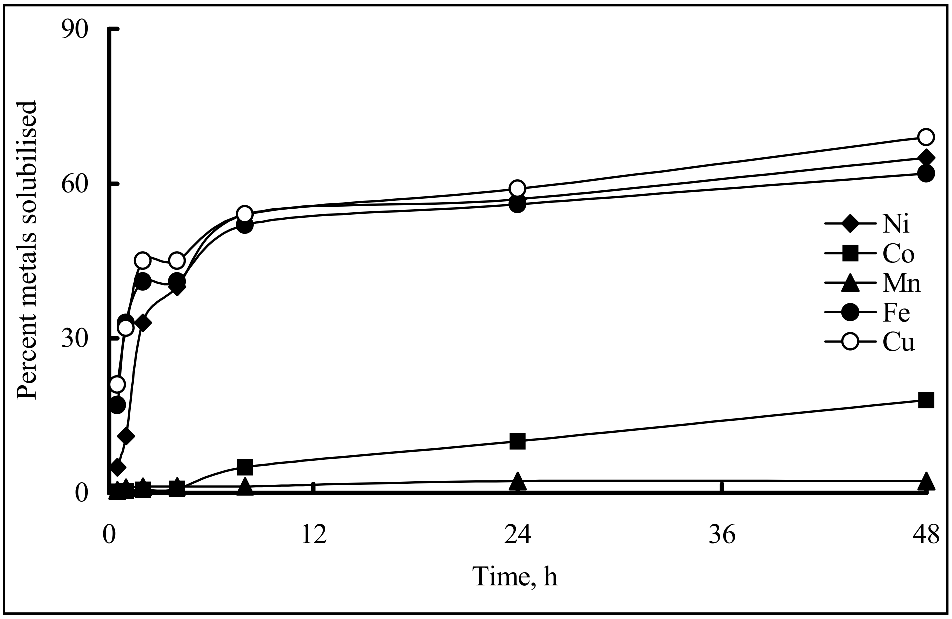

Figure 1. Leaching of the ocean manganese nodule (2%) in 1M H_2SO_4

3.1. Bioleaching with microorganisms

Another possible process is the treatment of ocean manganese nodules by microbial means. Yasuhiro et al. (1997) achieved 100% extraction of both copper and zinc within 4 days and high extraction of nickel (85%), cobalt (70%) and manganese (55%) in 10 days from ocean manganese nodule particle in presence of *Acidianus brierleyi* at 65°C.

Imai and Ghosh and Imai (1978, 1985) studied the leaching of manganese from manganese dioxide during the growth of *Thiobacillus thiooxidans* or *Thiobacillus ferrooxidans* using elemental sulphur as its substrate. *Thiobacillus* species were found to solubilize the oxide by producing sulphurous acid and reductive intermediates.

Typical results of bioleaching of ocean manganese nodule in the presence of *Thiobacillus thiooxidans* and sulphur-adapted *Thiobacillus ferrooxidans* are shown in Figure 2 (A-C).

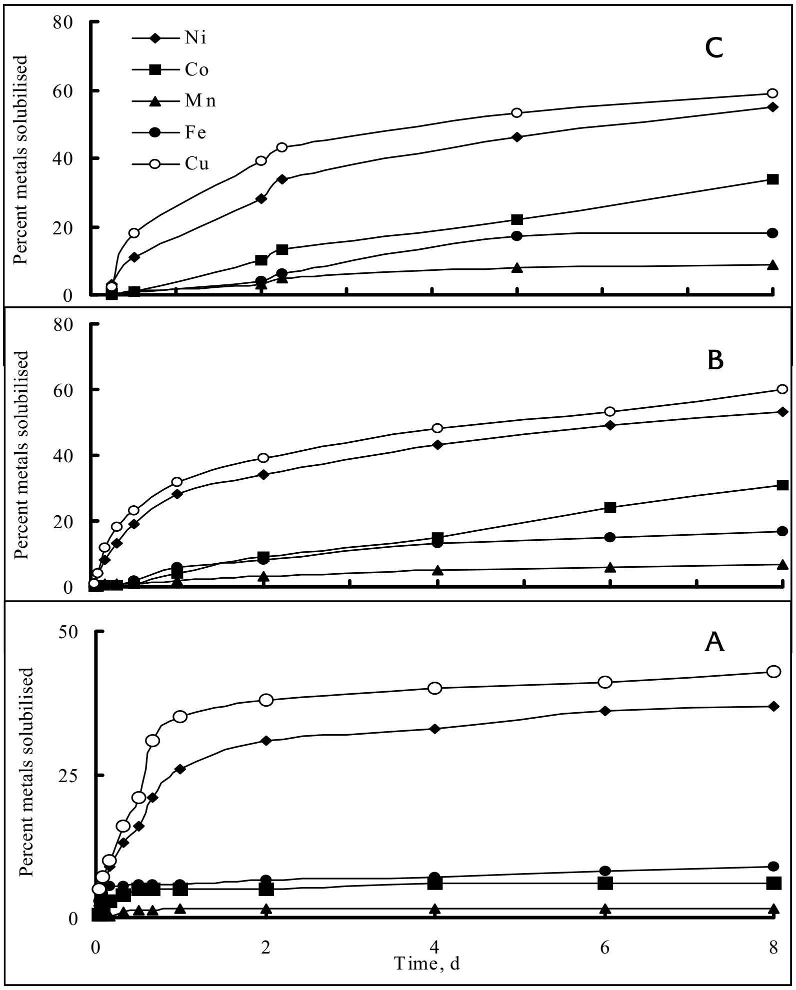

Figure 2. Bioleaching of ocean manganese nodule (2%) as a function of time at pH 2.0
(A) pH 2.0 H_2SO_4, (B) *Thiobacillus ferrooxidans* (S grown cells), (C) *Thiobacillus thiooxidans* cells

From the figure it can be seen that during chemical leaching in pH 2 sulphuric acid solution 37% Ni, 43% Cu, 6% Co and 9% of Fe were dissolved with negligible Mn in solution after 8 days. It can be also concluded that efficient dissolution of metals such as Cu, Ni, Co and Fe occur during growth of cells on elemental sulphur at the expense of acid produced by cells, whereas manganese dissolution increased only marginally.

It has been found that dissolution of all the above metals was almost the same during bioleaching of ocean manganese nodules in the presence of either *Thiobacillus thiooxidans* or *Thiobacillus ferrooxidans*.

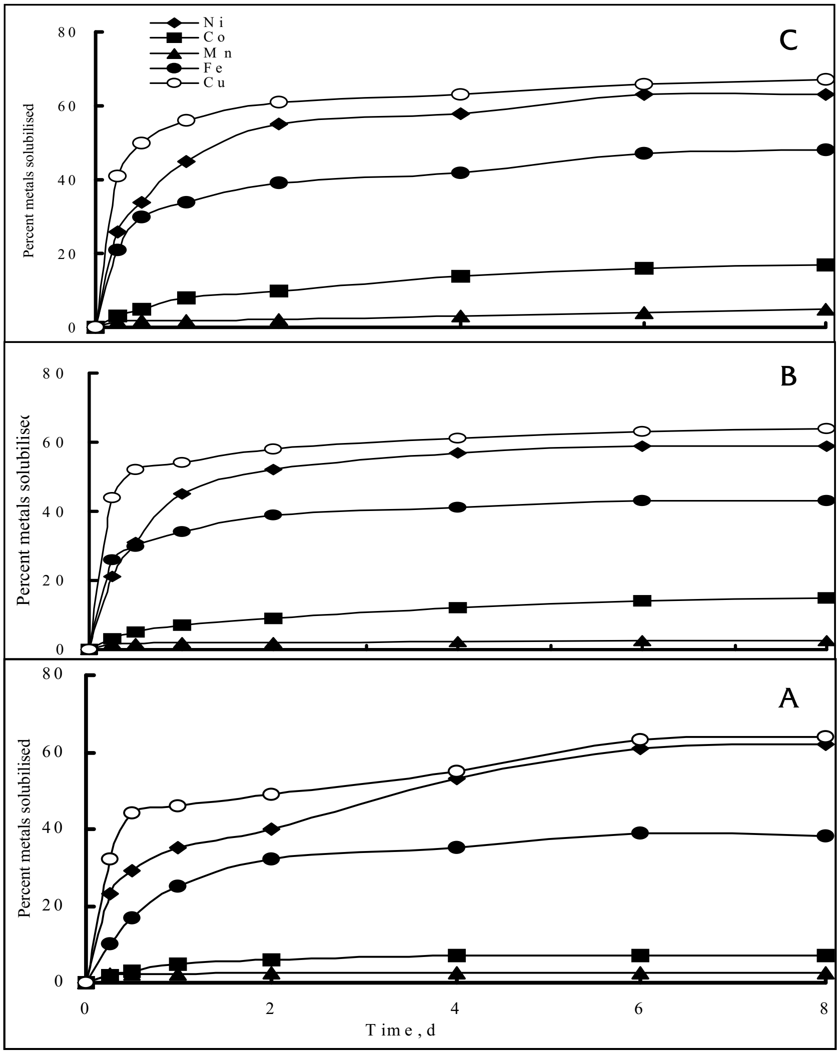

Figure 3. Bioleaching of ocean manganese nodule (2%) as a function of time at pH 0.5
(A) pH 0.5 H_2SO_4, (B) metabolite of *Thiobacillus ferrooxidans* (S grown), (C) metabolite of *Thiobacillus thiooxidans*

Results in Figure 3 (A-C) represent the extent of Cu, Ni, Co, Mn and Fe dissolution at different periods of time when the nodules were leached using metabolite of *Thiobacillus thiooxidans* or metabolite of *Thiobacillus ferrooxidans* at pH 0.5. In all the three cases the dissolution of all valuable metals was almost the same.

A lag phase in dissolution of metals during the initial stages due to lag phase of cell growth could be observed in bioleaching of nodules. Reductive intermediates of sulphur oxidation, such as thiosulphate and sulphurous acid which are biologically produced from the elemental sulphur due to bacterial oxidation effectively reduce manganic and iron oxides in the nodule releasing the interlocked metals.

3.2. Bioleaching in the presence of organic reducing agents

Sucrose behaves as a powerful reducing agent in acidic medium. Leaching of manganese nodule in ammoniacal medium using glucose as a reductant is reported (Das et al.; 1986). A 94% extraction yield of Mn^{2+} was been obtained at 50°C with 1M H_2SO_4 (0.98g acid/g of mineral) and 10g/l of sucrose (0.1g of sucrose/g of mineral) after 150min of treatment (Vegliò and Toro; 1994).

Results of bioleaching in the presence of metabolite, cells+metabolite+sulphur and cells alone with sucrose have been illustrated in Figures 4-6.

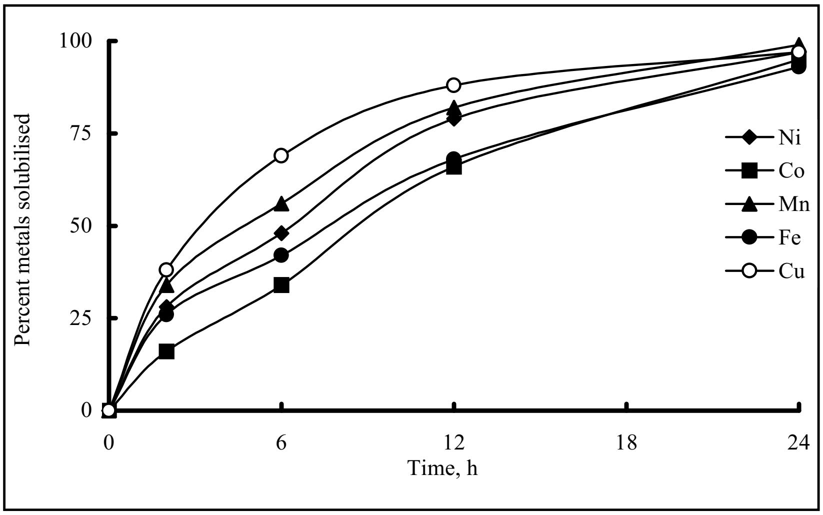

Figure 4. Bioleaching of ocean manganese nodules (2%) in the presence of metabolite of *Thiobacillus thiooxidans* containing 20g/l sucrose (pH 0.5)

It can be seen that all manganic and ferric oxides have been reduced which results in complete liberation of Cu, Ni and Co. Bioleaching with *Thiobacillus thiooxidans* alone in the presence of sucrose takes more time for reduction of Mn and Fe oxide in comparison to bioleaching in the presence of its metabolite.

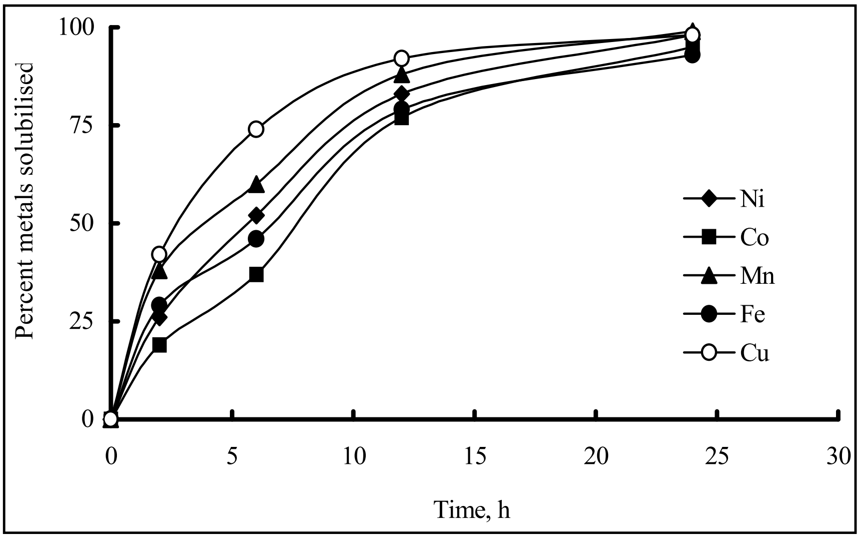

Figure 5. Bioleaching of ocean manganese nodules (2%) in the presence of a culture of *Thiobacillus thiooxidans*, (metabolite+cells) sulphur (10g/l) and sucrose (20g/l)

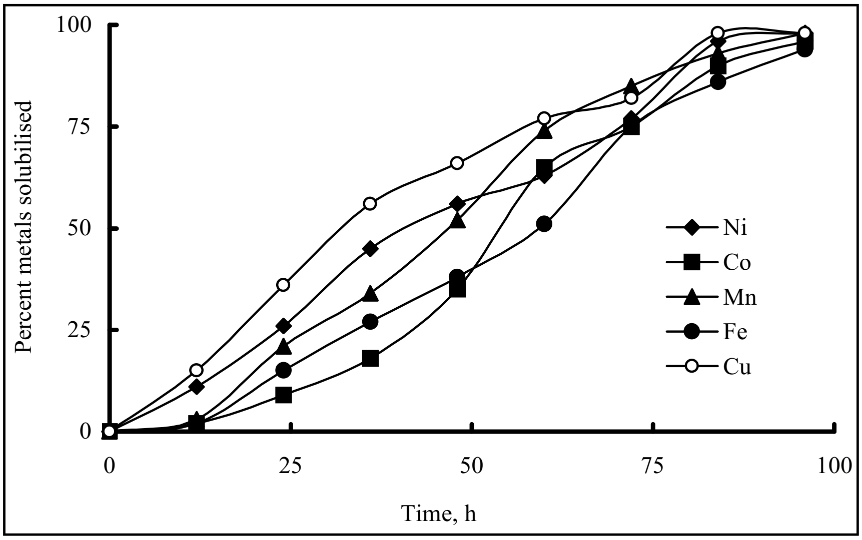

Figure 6. Bioleaching of ocean manganese nodules (2%) with cells of *Thiobacillus thiooxidans* alone in the presence of sulphur (10g/l) and sucrose (20g/l)

Results in Figure 5 corresponds to the condition where bacterial cells and their metabolic products are simultaneously present together during leaching, where as in tests corresponding to Figure 6, only bacterial cells (no metabolites) were present.

Better dissolution could be observed when both bacterial cells and their metabolites are available simultaneously. The reduction of manganic and ferric iron from ocean nodule in the presence of sucrose takes place according to following reactions.

$$24MnO_2 + C_{12}H_{22}O_{11} + 48H^+ \rightarrow 24Mn^{2+} + 12CO_2 + 35H_2O \quad (1)$$
$$12Fe_2O_3 + C_{12}H_{22}O_{11} + 24H^+ \rightarrow 12Fe^{2+} + 12CO_2 + 23H_2O \quad (2)$$

XRD and EDAX spectra of bioleached residues of the ocean manganese nodule sample in the presence of sucrose showed almost complete dissolution of Mn, Fe, Cu, Ni and Co with only peaks for Si remaining by.

3.3. Bioleaching tests with galvanic interactions and electrobioleaching

Galvanic interactions among different minerals are well known phenomena and based on electrochemical concept many galvanic leaching systems either for metal sulphide or sulphide-sulphide has been reported (Natarajan et al., 1983; Mehta et al., 1983; Joythi et al., 1989). Paramguru et al., (1996) have reported galvanic interaction between sphalerite and manganese dioxide through leaching and found a substantial increase in leaching of both of the minerals. Strong galvanic interaction was observed between sphalerite and manganese dioxide, the galvanic interaction predominating over the individual dissolution (self corrosion) rates. Paramguru et al. (1996) also examined galvanic interactions of the $MnO_2–FeS_2$ couple through polarization and leaching studies. Large galvanic currents observed between electrodes of this couple, increase further with an increase in H^+ concentration of the electrolyte. Devi et al. and Madhuchhanda et al (1999, 2000) have reported dissolution of metal values from deep-sea manganese nodule in HCl medium in presence of chalcopyrite. Kanungo (1999 a, b) reported leaching of the nodule in presence of pyrite, thereby effecting similar level of dissolution at considerably lower concentration of HCl and simultaneously avoiding iron dissolution. Reduction leaching of manganese nodules by nickel matte in hydrochloric acid was studied by Chen et al. (1992).

In galvanic bioleaching of ocean manganese nodule in the presence of pyrite, electrochemical interactions play a very prominent role. In order to understand the role of electrochemistry in galvanic bioleaching it is essential to consider both electrochemical as well as microbiological aspects. The involvement of galvanic effects in the bioleaching of some binary sulphide minerals combination has been reported previously (Natarajan et al., 1983; Mehta et al., 1983). Effect of *Thiobacillus ferrooxidans* during redox leaching of manganese nodules and nickel sulphide has been studied (Kai et al., 1996). Kinetic model for simultaneous leaching of zinc sulphide and manganese dioxide in the presence of iron oxidizing bacteria has also been reported (Takami et al., 2000). Kinetics of leaching manganese nodule in the presence of zinc sulphide mineral has been studied by Chen et al. (1995).

The role of added pyrite in the leaching of the ocean manganese nodule in 1M H_2SO_4 at three different ratios is illustrated in Figure 7.

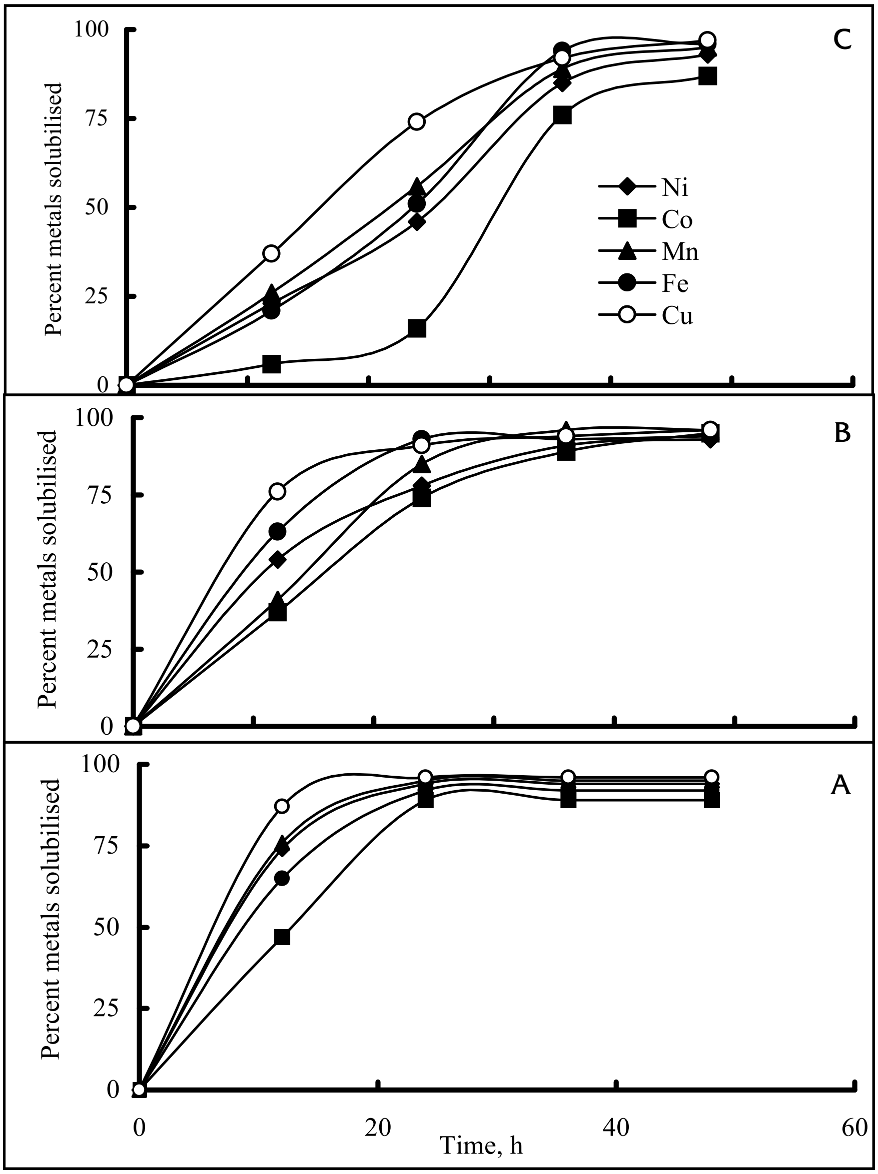

Figure 7. Leaching of ocean manganese nodule (2%) in 1M H_2SO_4 in presence of pyrite (A) ocean nodule:pyrite (2:10), (B) ocean nodule:pyrite (2:5), (C) ocean nodule:pyrite (2:2)

Comparing these results with those in Figure 1, the beneficial role of added pyrite could be readily seen. Higher amounts of pyrite in the mixture lead to increased leaching of the ocean manganese nodule.

Complete dissolution of all the metals in the nodule could be achieved in about 20 hours when the nodule:pyrite ratio was maintained at 2:10. Relatively more time will be required for higher extraction of the nonferrous metals when the amount of pyrite in the mixture is lowered.

The role of bacterial activity in the form of metabolic products and cells on the galvanic effects observed in the added presence of pyrite is illustrated in Figures 8-9.

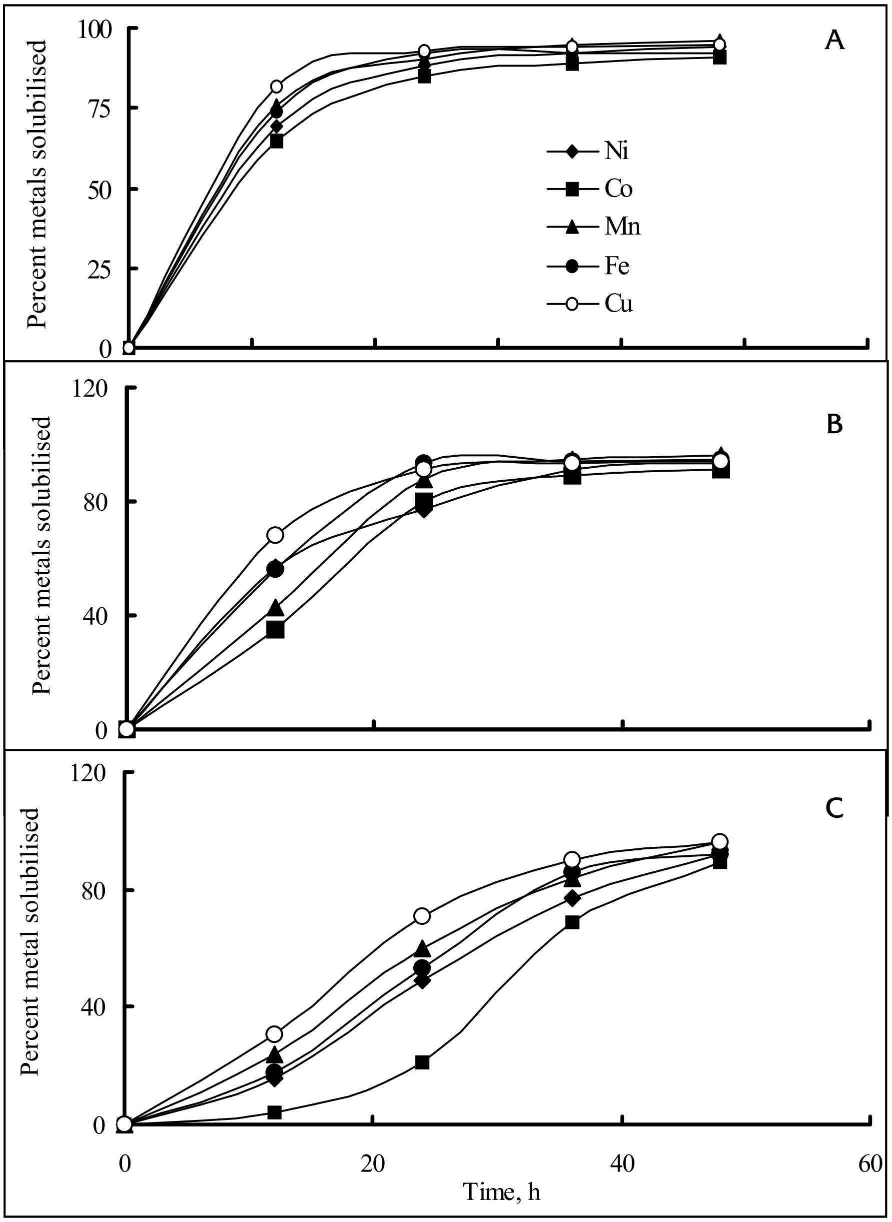

Figure 8. Leaching of ocean manganese nodule (2%) in metabolite+cells (10^{10}/ml) of *Thiobacillus thiooxidans*
(A) ocean nodule:pyrite (2:10), (B) ocean nodule:pyrite (2:5), (C) ocean nodule:pyrite (2:2)

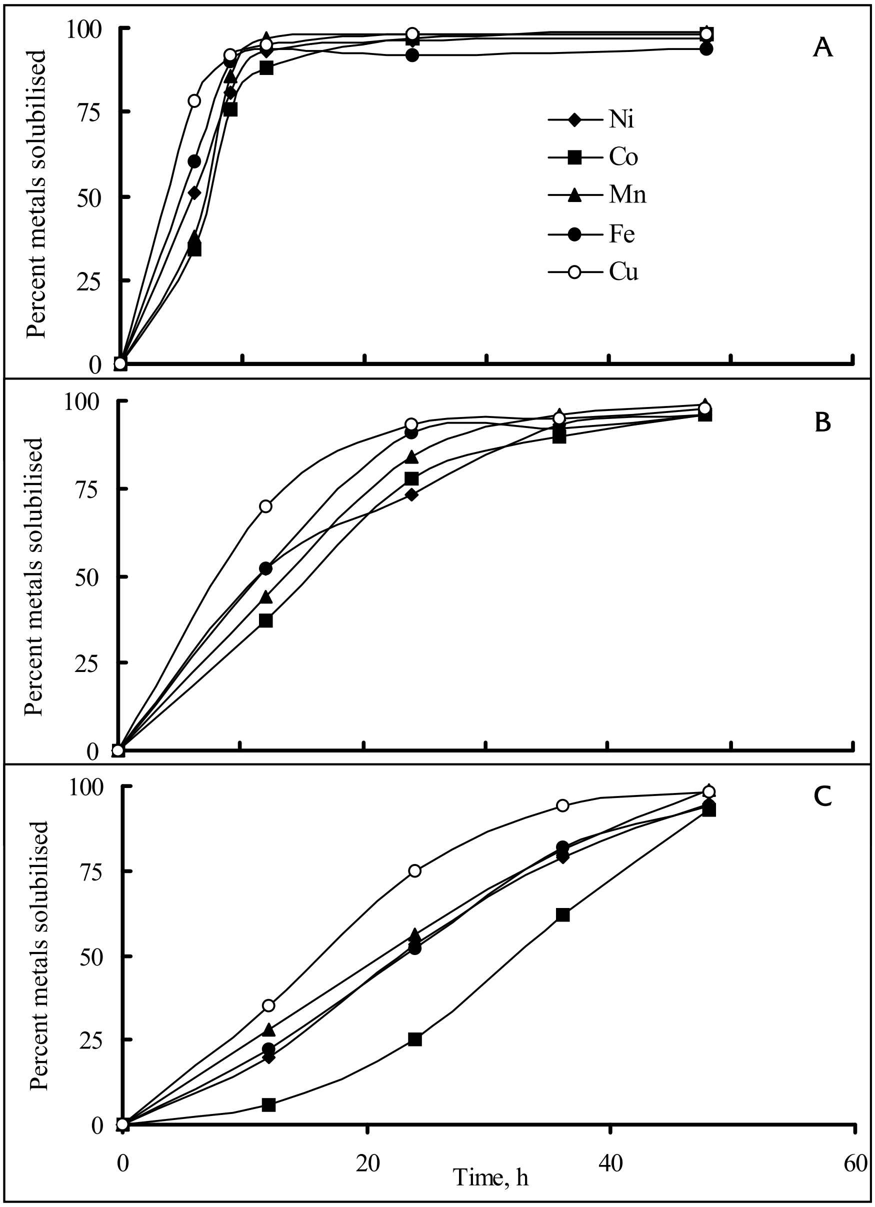

Figure 9. Leaching of ocean manganese nodule (2%) in metabolite+cells (10^{10}/ml) of *Thiobacillus ferrooxidans*
(A) ocean nodule:pyrite (2:10), (B) ocean nodule:pyrite (2:5), (C) ocean nodule:pyrite (2:2)

Bioleaching of ocean manganese nodule mixed with different ratios of pyrite in the presence of metabolite and cells of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* was performed. Almost complete reduction of manganic and iron oxides present in the ocean manganese nodule in the presence of pyrite due to the presence of acidic bacterial metabolites and cells also further promote galvanic interaction. In the absence of added pyrite direct bioleaching of the ocean manganese nodule did not result in such higher dissolution as observed in Figure 2.

The role of added pyrite in promoting the leaching of ocean manganese nodule can be seen in the light of galvanic interaction between anodic pyrite and cathodic manganic oxides (present in the nodule).

Anodic reaction:

$$FeS_2 + 8\,H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 16\,H^+ + 14e \qquad (3)$$

Cathodic reactions:

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \qquad (4)$$

$$MnOOH + 3H^+ + e^- \rightarrow Mn^{2+} + 2H_2O \qquad (5)$$

$$Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2Fe^{2+} + 3H_2O \qquad (6)$$

$$Fe(OOH) + 3H^+ + e^- \rightarrow Fe^{2+} + 2H_2O \qquad (7)$$

The above reactions provide a reducing environment by generation of ferrous sulphate and the reduction of manganic and ferric oxides liberate the interlocked nonferrous metal values such as copper, nickel and cobalt. In the presence of autotrophic bacteria and their metabolites, pyrite oxidation is further promoted, enhancing cathodic reduction of manganic and ferric oxides.

A reducing agent such as ferrous sulphate in solution can also be generated through electrochemical reduction of bacterially produced ferric ions. For example, *Thiobacillus ferrooxidans* oxidises ferrous ions to ferric ions and the bacterial metabolite contains upto 5g/l of ferric ions. Electrobioleaching of the ocean manganese nodule at –600mV (SCE) in the presence of metabolite of *Thiobacillus ferrooxidans* resulted in complete dissolution of all the metal values within 12 hours at a pH of about 0.5 which is illustrated in Figure10.

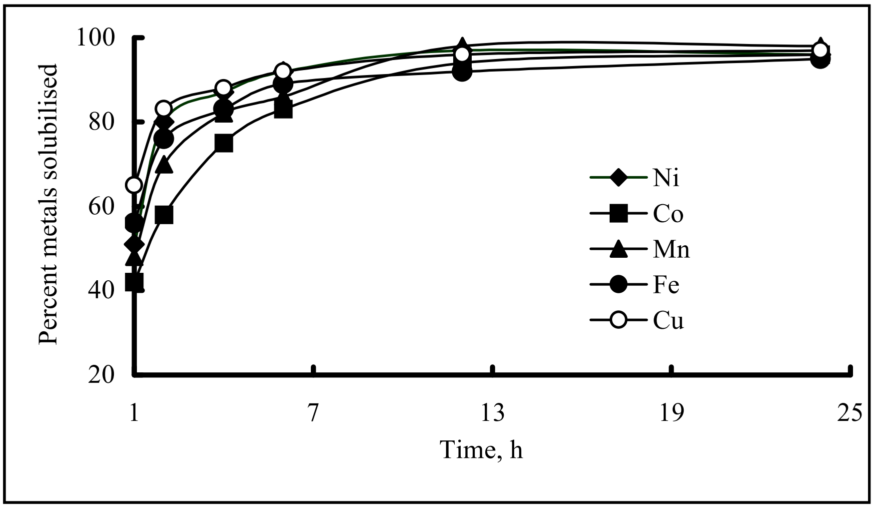

Figure 10. Electrobioleaching of the ocean manganese nodule (2%) at -600mV as a function time in the presence of metabolite of Fe grown *Thiobacillus ferrooxidans* at pH 0.5

At the above cathodic reduction potential, all the ferric ions in the bacterial metabolite could be reduced to the ferrous state besides bringing about reductive dissolution of the manganic, ferric and cobaltic oxides present in the ocean manganese nodule.

4. CONCLUSIONS

The following major conclusions can be made based on this study:

a) Bioleaching of ocean manganese nodules with cells of *Thiobacillus thiooxidans* in the presence of sucrose provides sufficient reducing conditions at lower pH to effectively reduce manganic and ferric oxides, facilitating easy acid dissolution of interlocked nonferrous metal values such as copper, nickel and cobalt.
b) Bioleaching of ocean manganese nodule with metabolite of *Thiobacillus thiooxidans* and metabolite+cells individually in the presence of sucrose shows faster reduction of manganic and ferric oxides in comparison to cells alone.
c) Reductive dissolution of the manganic and ferric oxides in the presence of reducing agents under acidic condition is proposed to be the major mechanism behind the liberation and release of interlocked nonferrous metal values.
d) Efficient dissolution of the valuable metals such as Cu, Ni, Co, Fe and Mn have been achieved from the ocean manganese nodule in the presence of pyrite in 1M H_2SO_4 due to galvanic coupling.
e) Complete recovery of valuable metals from ocean manganese nodule could be achieved in the presence of pyrite at the expense of acidic metabolite of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans.*
f) Reductive conditions in a bioleach system can also be achieved through application of cathodic potentials.

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