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Effect of thermal pretreatment on recovery of nickel and cobalt from Sukinda lateritic nickel ore using microorganisms

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Abstract−Experimental investigation made previously on microbiological leaching of nickel and cobalt from the laterite nickel ore of Sukinda Valley reveals that the recovery was not very much promising under any favorable conditions. Therefore, in order to improve the efficiency for bioleaching, the homogenized lateritic ore in palletized form is thermally pretreated by roasting at different temperatures. The parameters studied for the bioleaching experiments were the four types of pretreated ore which were roasted at different temperatures, i.e., 300 °C, 400 °C, 600 °C and 800 °C, in shake flask by using a mixed mesophilic acidophilic bacterial consortium consisting predominantly of the *Acidithiobacillus ferrooxidans* strain. It was observed that the pretreated ore at 600 °C with 10% (w/v) pulp density showed maximum recovery of nickel and cobalt, i.e., 59.18% (4.556 ppm) and 65.09% (0.546 ppm), using 10% (v/v) (2.5×10^8 cells/ml) consortium concentration at 1.5 pH, 30 °C, and 150 rpm after an incubation period of 31 days.

Key words: Bioleaching, *Acidithiobacillus ferrooxidans*, Lateritic Nickel Ore, Thermal Pretreatment, Palletized

INTRODUCTION

Bioleaching is no longer a promising technology but an actual economical alternative for treating specific mineral ores and also reducing the environmental impact of industrial activities [1]. This technique is slowly gaining importance in the field of waste treatment [2,3]. Therefore, it is an emerging technology with significant potential to add value to the mining industry as well as deliver attractive environmental and social benefits to the communities within which those companies operate [4]. For example, its application could result in the extraction of gold, copper, nickel, cobalt and zinc from sulphide ores without the emission of sulphur dioxide as occurs with conventional technologies. In scale up, processes like column and heap bioleaching runs for even more days to achieve maximum recovery [5]. Due to the increased consumption of diverse mineral products and progressive depletion of high-grade mineral deposits this biohydrometallurgy has come into perspective for extracting metals from low grade ores. The nickel and cobalt deposits of significant importance in India occur only in the lateritic profile developed over the ultramafic complexes in Sukinda Valley of Orissa. These are the weathered profiles of dunitic ultramafic rock bodies and occur as overburden material in association with chromite ore deposits. The concentration of nickel in the lateritic profile varies from a minimum of 0.15% to a maximum of 1.65% depending on the location of the deposit. Similarly, the concentration of cobalt in the lateritic profile ranges from 0.015% to 0.05%. The major challenge faced by these conventional techniques on low grade lateritic ores includes high processing cost, stricter environmental regulations on effluents and the requirement of high technological outlay. This bioleaching technique of lateritic nickel ore is economic and the cost economics will be high because we are avoiding a number of unit operations that are prevalent in pyro-hydrometallurgical routes. Therefore, microbiological leaching of low grade ores has drawn world-wide attention as a possible alternative.

Laterite is a highly weathered material rich in secondary oxides of iron, aluminum or both, and may contain quartz and kaolinite. Laterite often contains minor amounts of nickel, cobalt and chromium and high proportion of iron (III) oxide [6]. In Sukinda lateritic profile nickel is reported to be associated in goethite matrix and cobalt with manganese mineral phases [7]. The importance of the low-grade laterite ore to the future supply of nickel becomes obvious when one considers that 85% of the nickel reserves and a greater proportion of cobalt reserves are in laterite ores [8]. Studies have shown the amenability of laterite ores to leaching by heterotrophic microorganisms [9-11]. Organic acids (oxalic acid, citric acid, gluconic acid etc.) are excreted into the culture medium as metabolic products and subsequently dissolve heavy metals by forming salts and chelates [8]. Bioleaching studies were carried out to recover nickel, cobalt, manganese and iron from Sukinda chromite overburden using *Penicillium* sp., *Rhizopus arrhizus* and *Aspergillus niger* [12].

The objective of this work was to enhance nickel and cobalt recovery by a mechano-chemical and thermal pretreatment process of Sukinda lateritic nickel ore using a mixed mesophilic acidophilic bacterial consortium consisting predominantly of the *Acidithiobacillus ferrooxidans* strain.

MATERIALS AND METHODS

1. Lateritic ore Materials

Lateritic nickel ore samples used in this experiment were obtained from Sukinda Valley of lateritic profile, Orissa. The ore samples were homogenized by grinding and palletized in different size fractions. The palletized ore in 5 to 10 kg scale was thermally pretreated by roasting in a muffle furnace at different temperatures. The ther-

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Table 1. Chemical analysis of raw and thermally pretreated lateritic nickel ore

Types of thermally pretreated ore	Percentage (%)					
	Ni	Co	Fe	Cr	Mn	AI (Acid Insoluble)
Raw ore	0.62	0.032	47.86	4.02	0.35	8.6
Pretreated ore (300 °C)	0.75	0.043	55.85	4.14	0.43	7.4
Pretreated ore (400 °C)	0.76	0.04	55.87	4.20	0.50	7.9
Pretreated ore (600 °C)	0.77	0.042	55.88	4.21	0.52	7.8
Pretreated ore (800 °C)	0.79	0.045	55.86	4.20	0.54	7.7

mal pretreatment was at the rate of 10 °C per minute heating in the furnace up to the desired temperatures. Then the materials were cooled inside the furnace. So accordingly, the thermal pretreatment was done in preparation of different samples up to 300 °C, 400 °C, 600 °C and 800 °C separately with a constant heating rate of 10 °C per minute. Efforts were made to adopt the thermal pretreatment process to make changes in physical and mineralogical characteristics of laterite ore in order to improve the leaching efficiency.

The chemical analysis of the thermal pretreated lateritic ore pallet used for the bioleaching experiments is shown in Table 1.

2. Microorganisms

The microorganism used throughout the present work was a laboratory stock culture of a mixed mesophilic acidophilic bacterial consortium consisting predominantly of the *Acidithiobacillus ferrooxidans* strain. *A. ferrooxidans* has the ability to achieve optimum growth under strong acidic conditions (pH-2.5) by deriving energy for its metabolism from the oxidation of inorganic iron and reduced sulphur compounds. Bacterial growth was assessed by monitoring the iron oxidation rate in the $9K^+$ media [13]. The strain was screened for its ability to leach nickel and cobalt at a low pH of 1.5 at a constant temperature of 30 °C on rotary shaker at 150 rpm. The stock and pre-inoculum cultures were maintained in the same medium under similar conditions. The stock cultures were sub-cultured every week.

The standard medium for the growth of *A. ferrooxidans* is $9K^+$ media of Silverman and Lundgren [16] containing g/*l*: $(NH_4)_2SO_4$-3, KCl-1, $MgSO_4 \cdot 7H_2O$-0.5, KH_2PO_4-0.5, $FeSO_4 \cdot 7H_2O$-44 g/*l*. The pH in the medium was adjusted to 1.5 by adding 1 N sulphuric acid.

3. Mineralogy

The lateritic nickel ore samples which were thermally pretreated at different temperatures such as 600 °C and the raw lateritic ore respectively were analyzed high- resolution synchrotron based X-ray Diffractometer (XRD). The XRD analysis was done in order to know the major and minor minerals present in the ore material.

4. Bioleaching Technique

The leaching tests were carried out in 250 ml conical flasks each containing 10% (w/v) pulp density of thermally pretreated lateritic ore and 90 ml of $9K^+$ medium inoculated with 10 ml of bacterial culture containing 2.5×10^8 cells/ml. Prior to leaching, the microorganism was adapted to 10% (w/v) pulp density of lateritic nickel ore samples which were thermally pretreated at different temperatures such as 300 °C, 400 °C, 600 °C and 800 °C respectively. The pH of the samples was maintained at 1.5 by addition of 1 N sulphuric acid. Accordingly, control experiments were also performed with each set of experiments by the addition of $HgCl_2$.

The solutions inside the flask were agitated continuously in a rotary shaker at 150 rpm and incubated for a period of 31 days. After 31 days the experiments were terminated as there was no significant recovery of nickel and cobalt. At recorded intervals, i.e., 0, 7, 14 21, 28 and 31 days, samples were removed for chemical analysis and pH measurement. Before-sampling loss by evaporation was readjusted by adding sterile distilled water (2 ml before each sampling which is negligible). The sample volume was replaced by sterile culture medium. Leach suspensions were allowed to settle down, and from the clear upper part of the liquid, 2 ml was pipetted out. Accordingly, suitable dilutions were made with the help of distilled water. The metal concentrations in the leach solution were analyzed in a Perkin Elmer atomic absorption spectrophotometer (AAS).

RESULTS AND DISCUSSION

1. Ore Analysis

Chemical analysis of raw and thermally pretreated lateritic nickel ore is shown in Table 1. The raw lateritic nickel ore contains 0.62% Ni and 0.032% Co, the pretreated ore at 300 °C, 400 °C, 600 °C and 800 °C contains 0.75, 0.76, 0.77 and 0.79% Ni, respectively. Whereas, the pretreated ore at 300 °C, 400 °C, 600 °C and 800 °C contains 0.043, 0.04, 0.042 and 0.045% Co, respectively. While applying different temperatures it was observed that there was increase of different metals' contents as the temperature increased due to the structural loss of water from iron bearing hydrated minerals of goethite, ferrihydrites, etc., and to some extent from hydrated silicates like antigorite.

2. Leaching Potentialities *Acidithiobacillus ferrooxidans*

A mixed mesophilic acidophilic bacterial consortium consisting predominantly of the *Acidithiobacillus ferrooxidans* strain was progressively adapted to tolerate the thermally pretreated ores from 2% to 10% (w/v) pulp density. The microorganism was also adapted to tolerate nickel and cobalt concentrations from 0.25 to 1 g/L. The recovery of nickel and cobalt as a function of time at four different types of pretreated ore (300 °C, 400 °C, 600 °C and 800 °C)

Table 2. Percentage recovery of nickel and cobalt from pretreated ore

Types of thermally pretreated ore	Percentage (%) recovery in 31 days	
	Nickel	Cobalt
Pretreated ore-300 °C	21.03	22.68
Pretreated ore-400 °C	41.33	45.06
Pretreated ore-600° C	59.18	65.09
Pretreated ore-800 °C	29.03	33.16

in the 9K$^+$ medium and 10% (w/v) pulp density during bioleaching is shown in Table 2. Control experiments were also conducted for reasons of comparison. The amenability of this lateritic ore to biological recovery of nickel and cobalt was further supported by XRD data.

3. Effect of Thermally Pretreated Ore on Nickel and Cobalt Recovery

The lateritic nickel ore from Sukinda, India, is a low grade ore, which makes the recovery of metals difficult. The presence of metals in the lateritic ores, if proper care is not taken, may cause environmental pollution due to the leaching of metals by natural weathering processes (physicochemical or microbial). In such cases, microbial processes may prove efficient and environmentally friendly.

Leaching experiments made previously on microbial recovery of nickel and cobalt from the raw laterite nickel ore reveal that under any favorable conditions the recovery of nickel and cobalt from the ore samples was not very much promising [14]. In this study, the mixed mesophilic acidophilic bacterial consortium consisting predominantly of the *Acidithiobacillus ferrooxidans* strain was found more efficient in solubilizing nickel and cobalt with the thermally pretreated lateritic nickel ore at 600 °C. Nickel and cobalt recovery was maximum with thermally pretreated ore at 600 °C after an incubation period of 31 days with 10% (w/v) pulp density, pH 1.5, speed 150 rpm and temperature 30 °C and least at 300 °C. Under optimum conditions nickel recovery with thermally pretreated ore at 300 °C, 400 °C, 600 °C and 800 °C was 21.03, 41.33, 59.18 and

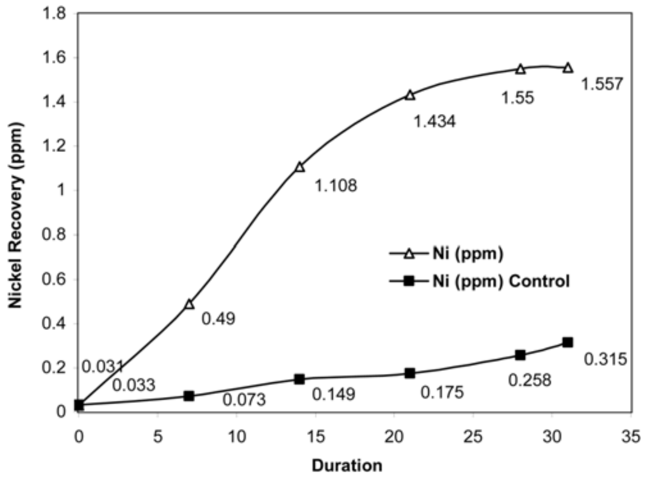

Fig. 1. Effect of thermally pretreated ore on nickle recovery using *A. ferrooxidans*.
Conditions-Pulp Density-10% (w/v), Roasting-300 °C, Inoculum size-10% (v/v), Temperature-30 °C, pH-1.5, Speed-150 rpm, Biomass-2.51×10^8 cells/ml, Duration-31 days.

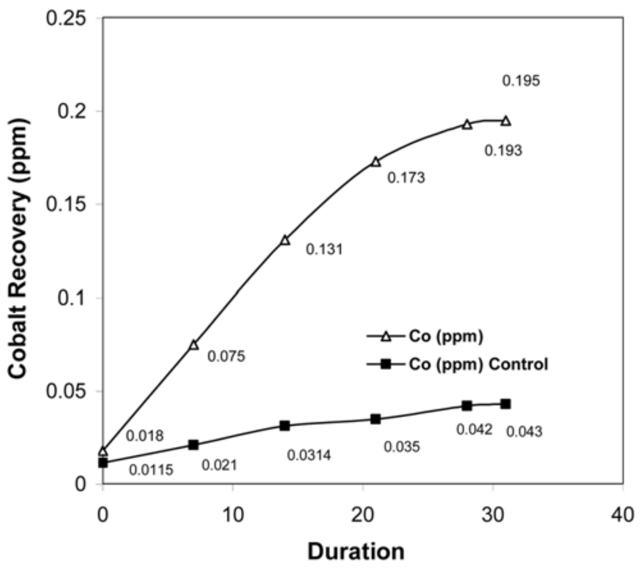

Fig. 2. Effect of thermally pretreated ore on cobalt recovery using *A. ferrooxidans*.
Conditions-Pulp Density-10% (w/v), Roasting-300 °C, Inoculum size-10% (v/v), Temperature-30 °C, pH-1.5, Speed-150 rpm, Biomass-2.51×10^8 cells/ml, Duration-31 days.

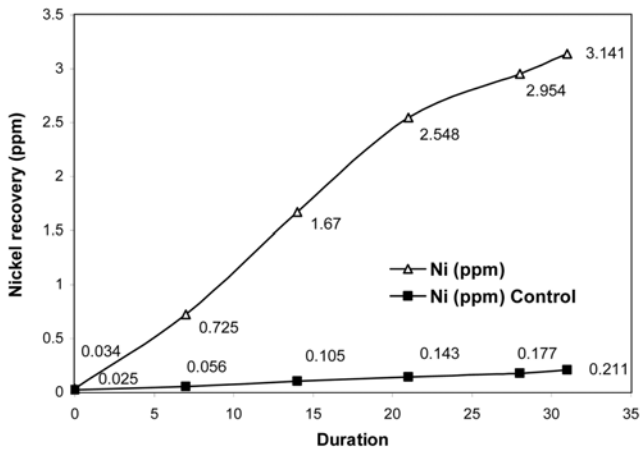

Fig. 3. Effect of thermally pretreated ore on nickel recovery using *A. ferrooxidans*.
Conditions-Pulp Density-10% (w/v), Roasting-400 °C, Inoculum size-10% (v/v), Temperature-30 °C, pH-1.5, Speed-150 rpm, Biomass-2.51×10^8 cells/ml, Duration-31 days.

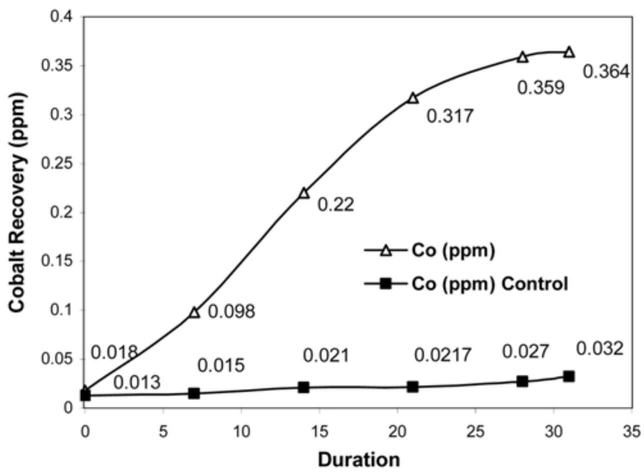

Fig. 4. Effect of thermally pretreated ore on cobalt recovery using *A. ferrooxidans*.
Conditions-Pulp Density-10% (w/v), Roasting-400 °C, Inoculum size-10% (v/v), Temperature-30 °C, pH-1.5, Speed-150 rpm, Biomass-2.51×10^8 cells/ml, Duration-31 days.

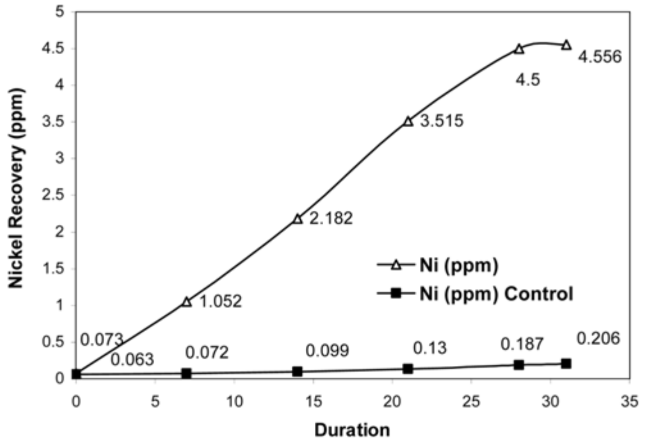

Fig. 5. Effect of thermally pretreated ore on nickel reovery using *A. ferrooxidans*.
Conditions-Pulp Density-10% (w/v), Roasting-600 °C, Inoculum size-10% (v/v), Temperature-30 °C, pH-1.5, Speed-150 rpm, Biomass-2.51×10^8 cells/ml, Duration-31 days.

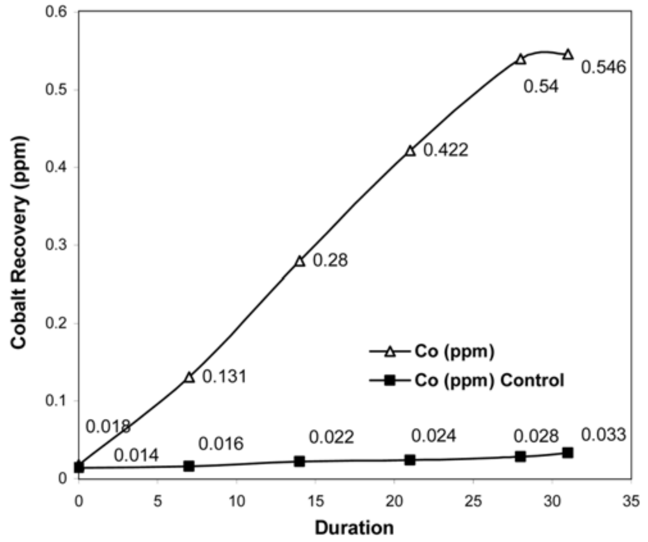

Fig. 6. Effect of thermally pretreated ore on cobalt recovery (ppm) using *A. ferrooxidans*.
Conditions-Pulp Density-10% (w/v), Roasting-600 °C, Inoculum size-10% (v/v), Temperature-30 °C, pH-1.5, Speed-150 rpm, Biomass-2.51×10^8 cells/ml, Duration-31 days.

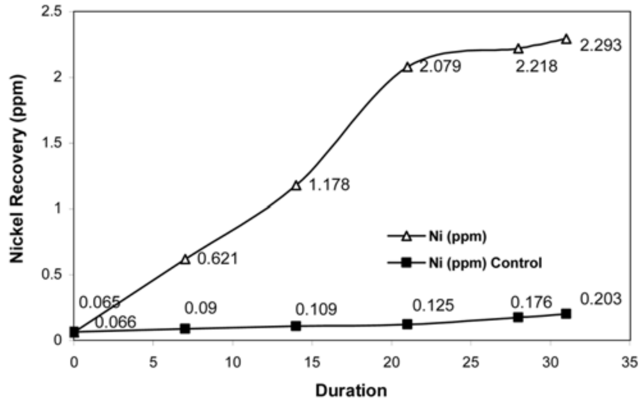

Fig. 7. Effet of thermally pretreated ore on nickel recovery using *A. ferrooxidans*.
Conditions-Pulp Density-10% (w/v), Roasting-800 °C, Inoculum size-10% (v/v), Temperature-30 °C, pH-1.5, Speed-150 rpm, Biomass-2.51×10^8 cells/ml, Duration-31 days.

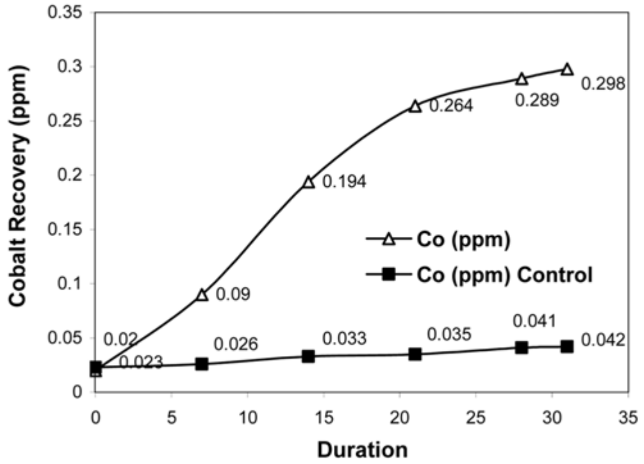

Fig. 8. Effect of thermally pretreated ore on cobalt recovery using *A. ferrooxidans*.
Conditions-Pulp Density-10% (w/v), Roasting-800 °C, Inoculum size-10% (v/v), Temperature-30 °C, pH-1.5, Speed-150 rpm, Biomass-2.51×10^8 cells/ml, uration-31 days.

29.03%, respectively (Table 2). The cobalt recovery with the same conditions using pretreated ore at 300 °C, 400 °C, 600 °C and 800 °C was 22.68, 45.06, 65.09 and 33.16%, respectively (Table 2). Figs. 1-8 show the nickel and cobalt recovery in terms of parts per million (ppm), and it was observed that the highest nickel and cobalt value seen in case of the pretreated ore at 600 °C was 4.556 ppm and 0.546 ppm, respectively. Least value nickel and cobalt value seen in case of the pretreated ore at 300 °C was 1.577 ppm and 0.195 ppm, respectively. Fig. 11 shows the effect of free acid in g/liter during the bioleaching process with respect to time. It was seen that initially the free acid was increased up to 21 days (9.433 g/liter) and after 21^{st} day it was decreased constantly to 6.738 g/liter. This might be the reason that nickel and cobalt are mostly occurring in the crystal lattices of goethite and to some extent in other oxides phases of iron. There is no separate mineral phase of nickel, and also the presence of it in low concentration and intricate association in goethite phase might make it very difficult to leach the metals. In the lateritic profile of Sukinda there is a complex association of cobalt with the manganese mineral phase, which makes it less amenable for leaching. But when the ore has been treated for a pretreatment process, which is a method of mechano-chemical and thermal operations where the lateritic ore undergoes physical and mineralogical characteristic change, the recovery of nickel from lateritic nickel ore is dependent on the type of mineralization. Detailed mineralogical studies, which were carried out on raw lateritic nickel ore and the thermally pretreated lateritic ore at 600 °C, indicated that there is no separate nickel bearing mineral phase in the raw lateritic nickel ore and the pretreated ore. Goethite, the main iron bearing phase, contains most of the nickel [15]. Because of such highly heterogeneous nature and complex

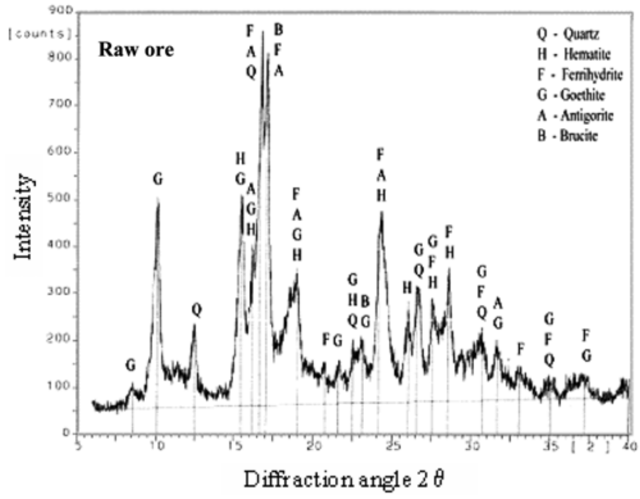

Fig. 9. XRD pattern of raw lateritic ore (Q-Quartz, H-Hematite, F-Ferrihydrite, G-Goethite, A-Antigorite and B-Brucite).

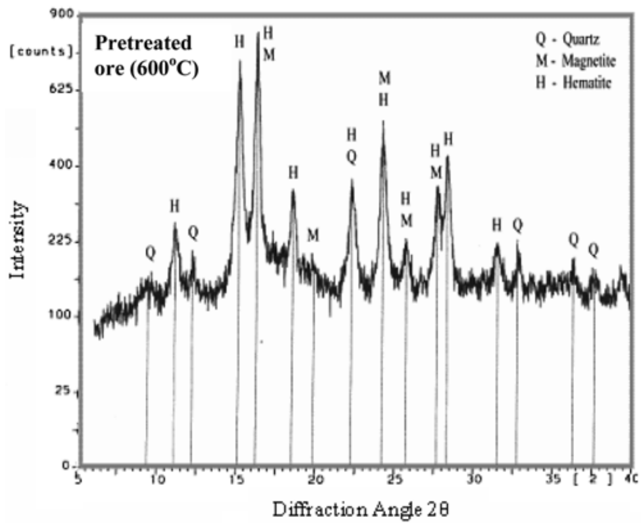

Fig. 10. XRD pattern of thermally pretreated ore at 600 °C (Q-Quartz, M-Magnetite and H-Hematite).

mode of association of nickel with goethite, mobilization of this element is very difficult with raw lateritic nickel ore. Nickel is reported to be associated with goethite matrix and cobalt occurs primarily in manganese mineral phases in Sukinda lateritic ore [7]. Roasting of ore at about 400 °C or above had been reported to convert goethite (FeOOH) into hematite (Fe_2O_3) and nickel may become exposed in micro pores and cracks developed in the particles, being more susceptible to leaching by the microorganisms [7,14]. Nickel is present in the form of NiO, and when it reacts with sulphuric acid provided in the medium forms nickel sulphate and water. Thermal pretreatment of ore at different temperatures helps in the conversion of goethite (FeOOH) into hematite (Fe_2O_3) and sulphuric acid when reacts with the hematite (Fe_2O_3) converts to ferric sulphate ($Fe_2(SO_4)_3$) and water. Simultaneously, NiO reacts with water and ferric sulphate (produced by the oxidation of ferrous ions by *Acidithiobacillus*) and this $Fe_2(SO_4)_3$ hydrolyzes to form ferric hydroxide (jarosite) and nickel sulphate which is water soluble. This helps in

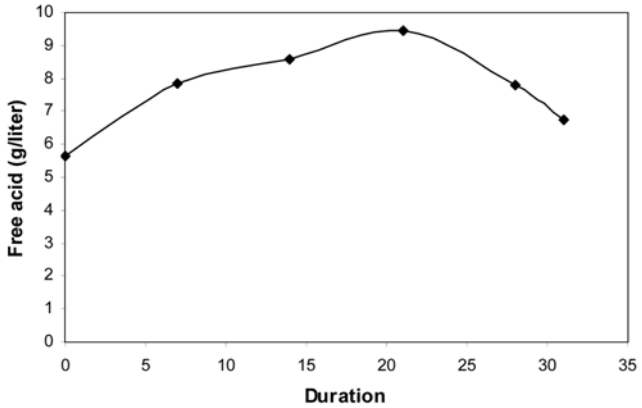

Fig. 11. Effect of free acid (g/liter) during the bioleaching of pretreated ore using *A. ferrooxidans.*

the enhancement of leaching percentage of the pretreated ores.

4. Mineralogy

The leaching of nickel from lateritic nickel ore is mainly dependent on the type of mineralization. In order to establish the effect of mineralogy, the raw lateritic nickel and the pretreated ore at 600 °C were examined by optical microscopy and synchrotron X-ray diffraction. Laterite is a highly weathered material in which the main nickel-bearing mineral is the hydrated iron oxide or goethite (FeOOH), as reported in a previous study [7]. The mineralogical studies indicated that there is no separate nickel bearing mineral phase in the lateritic nickel ore. Goethite is the main iron bearing phase, which contains most of the nickel in the raw lateritic nickel ore, and in the pretreated ore at 600 °C most of the goethite is being converted to hematite. The mineralogy of the raw lateritic ore in this study reveals the presence of goethite, ferrihydrites as major minerals, quartz as minor mineral phase and traces of hematite, brucite and antigorite. In the raw ore the abundance of minerals is as follows: ferrihydrites >goethite>quartz>hematite>antigorite>brucite (Fig. 9). In the pretreated ore at 600 °C the minerals present were hematite present as major, quartz as minor mineral phase and traces of magnetite were observed. The abundance of minerals in the pretreated ore is as follows: hematite>quartz>magnetite (Fig. 10). When thermal pretreatment is conducted at around 600 °C, goethite (FeOOH) gets converted to hematite (Fe_2O_3) and nickel may become exposed in micro pores and cracks developed in the particles, being more susceptible to leaching by the microorganisms. When the ore is heated because of dehydration the hydrated phases of iron are converted to oxides. Mostly in the first instance, the oxides of iron occur in the form of hematite, of which the content is maximum at 600 °C; other temperatures (below 600 °C) have comparatively less hematite phases. But when the temperature is increased above 600 °C further the hematite converts to magnetite.

CONCLUSIONS

The XRD analysis of raw lateritic nickel ore and pretreated ore at 600 °C revealed the conversion of goethite to hematite due to mechano-chemical and thermal operations. The mineralogical studies indicated that there is no separate nickel bearing mineral phase in the raw lateritic nickel ore and thermally pretreated ore at 600 °C.

In this study, a mixed mesophilic acidophilic bacterial consortium consisting predominantly of the *Acidithiobacillus ferrooxidans* strain was found more efficient in solubilizing nickel and cobalt with the thermally pretreated lateritic nickel ore at 600 °C. Under optimum conditions nickel and cobalt recovery with activated ore at 600 °C was 59.18 and 65.09% after an incubation period of 31 days.

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REFERENCES

1. H. L. Ehrlich, *Hydrometallurgy*, **59**, 27 (2001).
2. A. T. Bull, *Korean J. Chem. Eng.*, **18**, 137 (2001).
3. M. Mishra, S. Singh, T. Das, R. N. Kar, K. S. Rao, L. B. Sukla and B. K. Mishra, *Korean J. Chem. Eng.*, **25**, 531 (2008).
4. K. S. Rao, A. Mishra, D. Pradhan, G. R. Chaudhary, B. K. Mohapatra, T. das, L. B. Sukla and B. K. Mishra, *Korean J. Chem. Eng.*, (in press) (2007).
5. J. A. Brierley and C. L Brierley, *Hydrometallurgy*, **59**, 233 (2001).
6. E. O. Olanipekun, *International Journal of Mineral Processing*, **60**, 9 (2000).
7. L. B. Sukla and R. P. Das, *Transaction Indian Institute of Metals*, **40**, 351 (1987).
8. M. Valix, F. Usai and R. Malik, *Minerals Engineering*, **14**, 197 (2000).
9. K. Bosecker, In R. W. Lawrence, R. M. R. Branion and H. G. Ebner (Editors), *Fundamental and applied biohydrometallurgy*, Proceedings of the 6*th* International Symposium on Biohydrometallurgy, Vancouver, B.C., Canada, Elsevier, Amsterdam, August 21-24, pp. 367-382 (1985).
10. L. B. Sukla, R. N. Kar and V. V. Panchanadikar, In: Ayyana, C., (Ed.), *Recent trends in biotechnology*, Tata McGraw Hill Publishing Co., New Delhi, pp. 128-131 (1993).
11. L. B. Sukla and V. V. Panchanadikar, *Hydrometallurgy*, **32**, 373 (1983).
12. P. G. Tzeferis and S. Agatzini-Leonardou, *Hydrometallurgy*, **36**, 345 (1994).
13. E. Drobner, H. Huber and K. O. Stetter, *Applied Environmental Microbiology*, **56**, 2922 (1990).
14. S. Mohapatra, S. Bohidar, N. Pradhan, R. N. Kar and L. B. Sukla, *Hydrometallurgy*, **85**, 1 (2007).
15. C. Acharya, R. N. Kar and L. B. Sukla, *World Journal of Microbiology and Biotechnology*, **14**, 769 (1998).
16. M. P. Silverman and D. G. Lundgren, *Journal of Bacteriology*, **77**, 642 (1959).