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Microbial Recovery of Nickel and Cobalt from Pre-treated Chromite Overburdens of Sukinda Mines using *Aspergillus niger*

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Abstract

Aspergillus niger exhibits good potential in generating a variety of metal chelating and solubilization organic acids during cellular metabolism. In this context, the minor constituent metals like nickel and cobalt embedded in chromite overburdens (COB) of Sukinda mines have been exploited through bio-hydrometallurgical route for recovery of these metal values. XRD and EPMA analysis of COB reveals that initially nickel was intertwined in the goethite lattice while after pre-treatment (600°C), due to phase conversion of goethite to hematite leads to exposure of nickel particles into the micro-pores and cracks developed in the matrix. Hence, becoming more susceptible to attack by the fungal bio acids and accelerates metal dissolution. At a pulp density of 2 % (w/v) of pre-treated COB maximum nickel and cobalt recovered were 33.2 % and 82.4 % respectively after 24 days in shake flasks bioleaching using *A. niger*.

Key Words: *Aspergillus niger*, Chromite overburden, Nickel, Cobalt and Oxalic acid

Introduction

Chromite overburdens (COB) generated at Sukinda mines, Orissa, India, are known as only nickel laterite deposits. Laterites are oxide ores widely distributed in the tropical regions. They were formed during laterization, a weathering process of ultramafic rocks which is favoured by warm climate and abundant rainfall. In India, particularly in Sukinda mines Orissa, a huge amount of overburden is generated during chromite ore mining, which having 0.5- 1.0 % nickel and 0.03-0.04 % cobalt [1]. The existing mineral processing routes for nickel recovery from laterite are high pressure acid leaching, Caron process, ferronickel and nickel matte smelting techniques. These processes involve higher energy utilisation and operational costs [2]. In this regard an effective technology for recovery of such valuable metals from these chromite overburdens is highly desirable that can address the aforesaid challenges. Therefore bioleaching can be an alternative process for economic and environment friendly extraction of metals. With a view to extract substantial amount of metal values from chromite overburdens, pre-thermal activation of chromite overburden was carried out prior to leaching. The thermal pre-treatment of chromite overburden have significantly influence on nickel and cobalt recovery through bioleaching [3]. The thermal activation changes the mineral structure and brings the mineral phase transformation by dehydroxylation of the goethite matrix in raw chromite overburden [4, 5].

Bioleaching of oxide and silicate ores require heterotrophic microorganisms which are able to produce organic acids, mainly oxalic acid, citric acid, gluconic acid, tartaric acid, and pyruvic acid. *Aspergillus* and *Penicillium* are the most widely used important filamentous fungi for the extraction of metals from oxide ores [6, 7]. Metal leaching by heterotrophic microorganisms generally involves an indirect process through microbial production of organic acids, amino acids and other metabolites. Four mechanisms have been reported to be involved during fungal bioleaching: (i) Acidolysis (ii) Complexolysis (iii) Redoxolysis and (iv) Bioaccumulation [8].

In this present study, an attempt has been made to study the effect of thermal pre-treatment of the chromite overburden on the recovery of nickel and cobalt using fungal strain *A. niger.*

Materials and Methods

Overburden Samples

Chromite overburden samples were obtained from major chrome deposits of Sukinda Mines, Orissa, India. In this overburden, nickel is associated with the goethite matrix and cobalt is associated with the manganese phase. Laterite is a highly weathered material rich in hydrated iron oxide goethite α-FeO (OH) or $Fe_2O_3.H_2O$, or both but devoid of bases and primary silicates and may contain abundant quartz and kaolinite. It contains minor amount of nickel, cobalt, and chromium [9].

For the experimental purpose the raw chromite overburden (COB) samples were thermally pre-treated at 600°C for 5 hours to convert the goethite to hematite in order to release the nickel from its goethite matrix [1, 9]. The chemical analysis of the raw and the pre-treated chromite overburdens are shown in Table 1.

Table 1. The chemical composition of different types of chromite overburdens

Types of Chromite Overburden	Ni %	Co %	Fe %	Cr %	Mn %
Raw Sample	0.99	0.03	48.88	2.59	0.21
Pre-treated Sample	1.02	0.04	50.85	3.65	0.35

Fungal Strain and Growth Conditions

A laboratory stock culture of *Aspergillus niger*, was used for this study. Bromofield media containing (g/L) of $MgSO_4$ $7H_2O$-0.75, KH_2PO_4- 0.25, $(NH_4)_2SO_4$- 0.25, yeast extract- 1, sucrose-20 used for the growth of the fungi. The initial pH of the media was 6.8. The fungal strains were adapted to the ore by repeatedly growing them in Bromofield media containing chromite overburdens. Fungal cultures were preserved at 4˚C in potato dextrose agar slants. The spore suspension of 5 to 7 days old culture was used as inoculums.

Leaching Experiments

A.niger mediated leaching experiments were carried out with 2.0% (w/v) raw & pre-treated chromite overburdens in 250ml Erlenmeyer flask containing 90 ml of sterilized Bromofield medium, 10 ml of fungal spore suspension as inoculum. The chromite overburdens were crushed to an average size of 63-75 micron prior to leaching. Flasks were kept in rotary shaker (Khuner, Switzerland) at 150 rpm, 30^{o}C for a period of 24 days. Aseptic conditions were maintained throughout the experiment.

Liquid samples were drawn at periodic intervals and filtered and subjected to atomic absorption spectroscopic analysis for nickel and cobalt. Organic acids present in the fungal culture filtrate were identified and quantified by HPLC (Agilent technologies, Waldbronn Analytical Division, Germany).

Mineralogical Studies

The compositional and distributional map of different elements in chromite overburdens was determined under electron probe micro analyser (JEOL, JXA-8100). The X-ray diffraction study was carried out by means of Phillips Diffractometer (PW3710) with a radiation operating at 40kV and 30mA. Fourier-transform infrared (FT-IR) spectral studies were carried out with a Perkin Elmer (Model Spectrum 1) spectrophotometer in the range between 4000–400 cm^{-1}, with a resolution of 2 cm^{-1}. Powdery samples were compressed into potassium bromide (KBr) pellets by applying a pressure of 300kg/cm^2 for the FT-IR measurements. The transmission electron microscope (TEM) investigation was carried out using microscope (FEI, TECNAI G^2) 20 TWIN, operating at 200 KV equipped with a GATAN CCD camera. All the samples were dispersed in ethanol and sonicated and subsequently drop of it was put on a copper grid for TEM measurement.

Results and Discussion

Mineralogical studies of chromite overburdens

The nickel and cobalt from chromite overburdens are mainly dependent on the type of mineralization. In order to establish the effect of mineralogy on nickel and cobalt recovery, the raw lateritic nickel and pre-treated chromite overburden at 600^{o}C were examined by, EPMA,X-ray diffraction and FTIR spectroscopy& TEM.

Electron Probe Micro Analyzer (EPMA) Study

In the original chromite overburden sample Ni and Co are observed to be confined within Fe and Cr-phases. In case of the pre-treated overburden sample (at 600^{o}C) most of the goethite gets converted to hematite. The compositional map of pre-treated sample shows more diffused Ni and Co in compare to original chromite overburden. (Figure: 1 a & b)

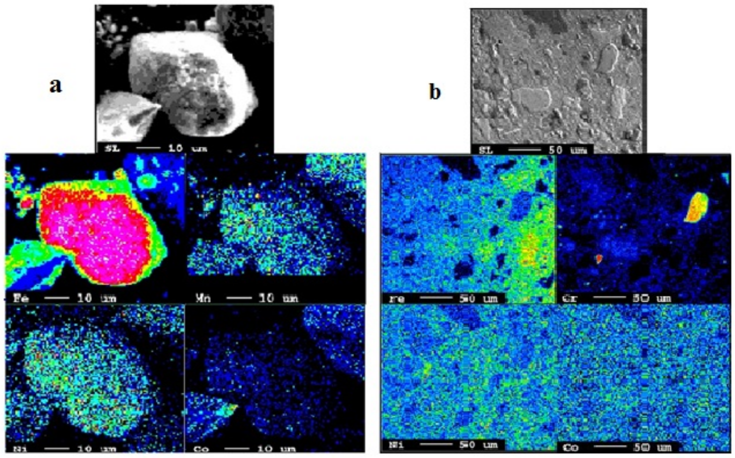

Figure 1. Composition map of a grain in raw chromite overburden sample studied under EPMA. (a) Raw chromite overburden. (b) Pre-treated chromite overburden

X-ray diffraction study

X- ray diffraction analysis reveal the presence of goethite, ferrihydrites, as major minerals, quartz as minor mineral phase and traces of hematite, brucite and antigorite in the chomite overburden sample. In the pre-treated (600°C) chromite overburden minerals present were hematite as major and quartz as minor mineral phase with traces of magnetite. When thermal pre-treatment is conducted at around 600°C, goethite (FeOOH) gets converted to hematite (Fe_2O_3), cracks developed in ore particles so that nickel may become exposed in micropores and becomes more susceptible to leaching by microorganisms and organic acids.

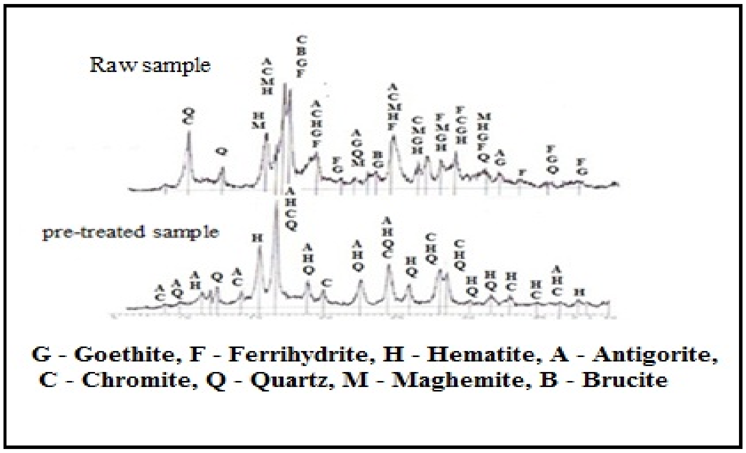

Figure 2. X- ray diffraction spectra of raw and pre-treated sample chromite overburdens

FT-IR study

The raw chromite overburden and thermally pre-treated chromite overburdens were analysed by FT-IR spectroscopy, the FT-IR analysis of raw chromite overburden shows the goethite peaks characteristics, in case of pre-treated chromite overburdens the characteristics peaks of hematite were found. The hematite particles which formed by dehydration and reordering of the internal bonds of the goethite iron oxide samples during the thermal activation were spheroidal. Hematite formed during thermal treatment of the chromite overburden gave broad IR band centred at 533 and 454 cm^{-1} (Fig.3-b)and similar type of vibration can be seen in FT-IR spectroscopy of the natural hematite (Fig.3-c). Similar peaks were observed by Vempati et al [10].

The decrease in band intensity and shift in band centre from 3155 cm^{-1} to 3400 cm^{-1} is indicative of the transformation of structure from goethite to hematite. While the 2924 cm^{-1} band in the newly formed hematite (Fig.3c and 3b) is the vibration of non-stoichiometric hydroxyl units that transferred directly from goethite to hematite [11, 12]. This structural alteration indicated by hydroxyl units is obviously observed only in the FT–IR spectra compared with the XRD technique.The band at 3409 cm^{-1} (Fig. 3b) in the hydroxyl stretching region remained at 3155cm^{-1} after the completion of goethite–hematite transformation. This indicates that goethite is altered to hematite without intermediate phases and the newly formed hematite inherited the remaining non-stoichiometric hydroxyl units from the precursor goethite.

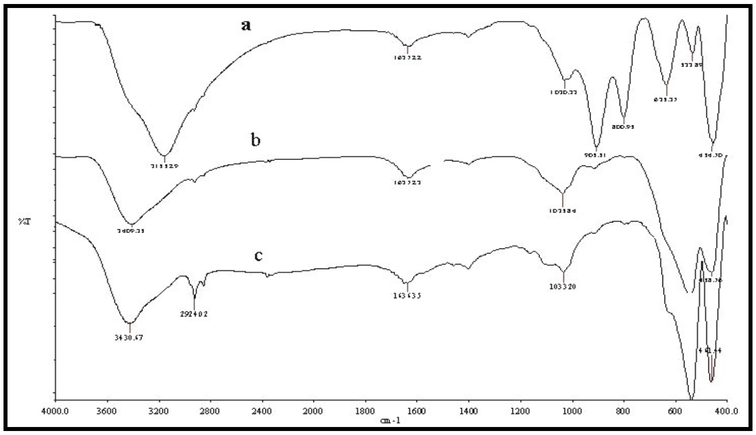

Figure3. FT-IR-spectra of (a) Raw chromite overburden (b) Pre-treated chromite overburden (c) Natural hematite Fe_2O_3

Transmission Electron Microscopy (TEM) Study

The TEM investigation reveal the fine nature of the constituent minerals and their mutual arrangements which gives a lot of porous spaces to the agglomerates in roasted chromite overburden samples.TEM study was conducted with roasted chromite before and after leaching which showed that hematite consisted of a mixture of acicular crystals with rounded ends due to surface diffusion (Fig. 4b &4c). In case of roasted overburden before leaching the rounded ends were more as compared to after leaching. These crystals vary from 90-150 nm in length and their width varying from 6-15 nm. The transmission electron microscopic study reveals that, during leaching nickel was solubilised from iron matrix of pre-treated chromite overburdens. The porous mineral matrix of leached residue explains that, release of nickel from the iron matrix. The TEM investigation support the experimental finding that, the enhanced recovery of nickel and cobalt in case of roasted overburden is due to highly porous material with increased surface area (Figure 4c). The shape of the pores vary from spherical to sub-spherical in shape while in some cases the pores have merged to form larger pores. The size of the pores varies from 10-30 nm in size.

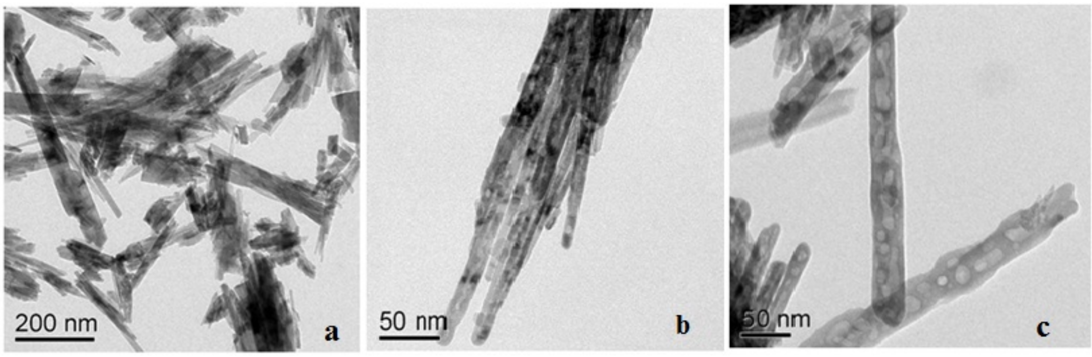

Figure 4. Transmission electron microscopic structure of (a) raw chromite overburden before leaching, (b) Pre-treated chromite overburden before leaching, (c)Pre-treated chromite overburden after leaching

Leaching Study

About 33.2 % of nickel and 82.4 % cobalt were recovered from pre-treated COB in 24 days through *A. niger* mediated bioleaching (Figure-5). Where as in case of raw chromite overburden the nickel and cobalt recovery percentage was almost negligible in compared to the thermally pre-treated chromite overburden. The pH during leaching dropped down from 6.8 to 2.8 (Figure-6). Prominent carboxylic acids such as oxalic acid and citric acid were detected in HPLC in culture filtrate of *A. niger* after maximum utilization of the sucrose by *A. niger.* Analysis for organic acid content carried out with triplicate samples, an about 0.76 - 0.81 g/l oxalic acid and 0.72- 0.76 g/l citric acid was detected in the culture filtrate of *A. niger*

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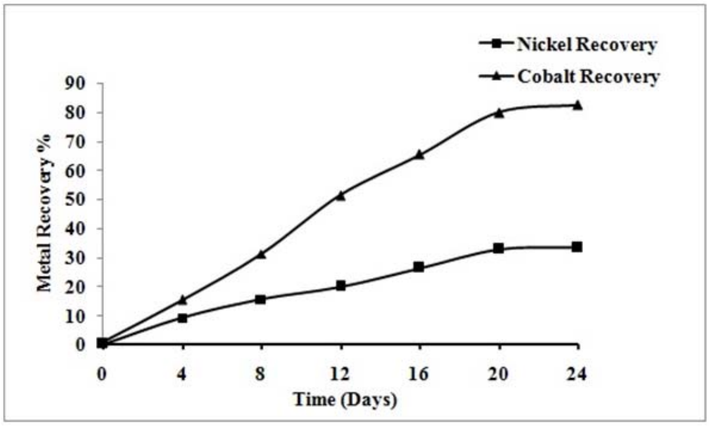

Figure 5: Nickel and Cobalt recovery from pre-treated chromite overburdens using *Aspergillus niger*

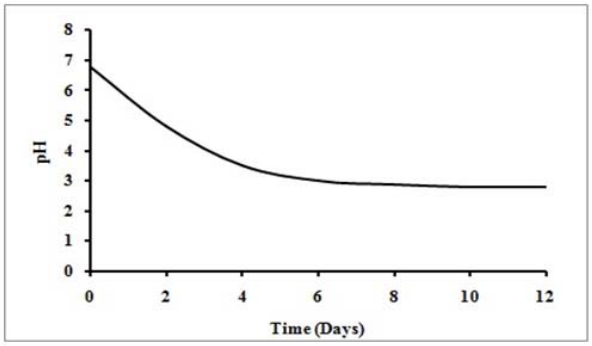

Figure-6: pH change during the *A. niger* culture

Microorganisms during metabolism, converts the glucose or other carbohydrates into variety of products including organic acids which leads to lowering of pH .The production of acid helps in partially dissolving the goethite matrix thereby releasing the nickel into the solution.The fungal bioleaching processes are mediated through the chemical attack of secreted organic acids on the ores [1, 8]. The acids usually have dual effect of increasing metal dissolution by lowering the pH and increasing the load of soluble metals in solution by complexing/chelating into soluble organo-metallic complexes.

Acid Production

$$\text{Glucose / Sucrose} \xrightarrow{\text{Fungus}} \text{Oxalic / Citric acid} \quad \text{(Eq.1)}$$

$$\text{Oxalic/citric acid + Ni/Co} \longrightarrow \text{Ni/Co-oxalate/Citrate complex} \quad \text{(Eq.2)}$$

Extraction of Nickel and Cobalt totally depends upon the mineral phases with which these valuable metals associated in COB. Enhanced extraction of nickel and cobalt was obtained in case of the pre-treated COB, compare to raw COB during bioleaching. As majority of nickel is present in the lattice of the iron oxide matrix of COB, the extraction of the nickel during leaching is directly proportional to the dissolution of iron matrix by carboxylic acids secreted by *A. niger*. The thermal treatment of COB has significant influence on nickel and cobalt recovery [3]. The thermal activation changes the mineral structure and brings the mineral phase transformation by dehydroxylation of the goethite matrix [5].

The higher extraction of the nickel achieved from pre-treated chromite over burden due to dehydroxilation of the nickel bearing mineral phase goethite in raw chromite overburden to hematite via topotactic modification. The phase conversion from goethite to hematite leads to exposure of nickel particles into the micro-pores and cracks developed in the matrix, hence becoming more susceptible to attack by the fungal bio acids and accelerates the dissolution. Enhanced extraction of nickel and cobalt obtained during leaching processes from pre-treated chromite overburden not only due to increased porosity and surface area, but also the change in reactivity of the ore due to extensive dehydration and dehydroxylation of various hydrated oxide minerals. These factors favours the higher solubility of iron phase present in pre-treated chromite over burden in compare to original chromite overburden.

Conclusion

The aforesaid discussion may be concluded that the dissolution of nickel and cobalt from the chromite overburden, Sukinda by fungal strain *A. niger*is an indirect process of bioleaching. The XRD analysis of chromite overburden showed nickel present in absorbed state within the goethite matrix whereas in pretreated overburden revealed conversion of goethite to hematite due to thermal activation at 600°C under normal atmospheric conditions.This result in increased leach-ability might be due to increased porosity, increased surface area and change in reactivity of the ore due to extensive dehydration and dehydroxylation of various hydrated oxide minerals. Efficiency for production of organic acid of *A. niger* was also tested. TEM analysis of the leached samples shows that during progressive leaching nickel dissolute into the solution leaving a porous space in the matrix. Nickel dissolute from the core of the hematite matrix in the pre treated COB by forming organo-metallic complex (Ni-oxalate/ Ni-citrate). It was observed that 33.2 % of nickel and 82.4 % of cobalt was recovered from pre treated COB at 2.0% pulp-density with 10% (v/v) fungal inoculum at 30°C for a duration of 24 days in shake flask scale.

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References

[1] Mohapatra, S., S. Bohidar, N. Pradhan, R.N. Kar and L.B.Sukla. 2007. Microbial extraction of nickel from Sukinda chromite overburden by Acidithiobacillus ferrooxidans and Aspergillus strains. Hydrometallurgy. 85: 1–8.

[2] Deepatana, A., J.A. Tang and M. Valix. 2006. Comparative study of chelating ion exchange resins for metal recovery from bioleaching of nickel laterite ores. Minerals Engineering. 19: 1274–1279.

[3] Valix, M. and W.H. Cheung. 2002. Study of Phase Transformation Of Laterite Ores At High Temperature. Minerals Engineering. 15 (8): 607 – 612.

[4] Landers, M. and R.J. Gilkes. 2007. Dehydroxylation and dissolution of nickeliferous goethite in New Caledonian lateritic Ni ore. Applied Clay Science. 35: 162–172.

[5] Jinhui, L., L. Xinhai, H. Qiyang, W. Zhixing, Z. Youyuan, Z. Junchao, L. Wanrong and L. Lingjun. 2009. Effect of pre-roasting on leaching of laterite. Hydrometallurgy. 99: 84 - 88.

[6] Franz, A., W. Burgstaller, and F. Schinner. 1991. Leaching with P. simplicissimum: influence of metals and buffers on proton extrusion and citric acid production. Appl. Environ. Microbiol. 57: 769–774.

[7] Bosecker, K. 1997. Bioleaching: metal solubilization by microorganisms. FEMS Microbiol. Rev. 20: 591–604.

[8] Burgstaller,W. and F. Schinner. 1993. Leaching of metals with fungi, mini review. J. Biotechnol. 27: 91–116.

[9] Sukla, L.B. and R.P. Das. 1987. Kinetics of nickel dissolution from roasted laterites. Trans. Indian Inst. Met. 40: 351–353.

[10] Vempati, R.K., R.H. Loeppert, H. Sittertz-Bhatkar and R.C.Burghardt. 1990. Infrared vibrations of hematite formed from aqueous – and dry- thermal incubation of Si-containing ferrihydrites. Clays and Clay Minerals. 38 (3): 294-298.

[11] Ruan, H.D., R.L. Frost, J.T. Kloprogge and L. Duong. 2002. Infrared spectroscopy of goethitedehydroxylation. II. Effect of aluminium substitution on the behaviour of hydroxyl units. Spectrochimica Acta Part A. 58: 479–491.

[12] Ruan, H.D., R.L. Frost, J.T. Kloprogge and L. Duong. 2002. Infrared spectroscopy of goethitedehydroxylation: III. FT-IR microscopy of in situ study of the thermal transformation of goethite to hematite. Spectrochimica Acta Part A. 58: 967–981.