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Leaching of copper converter slag with *Aspergillus niger* culture filtrate

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Leaching of copper converter slag of M/s Hindustan Copper Ltd, Ghatshila (Bihar, India) was carried out using *Aspergillus niger* culture filtrate. The effects of the duration of leaching, temperature, pulp density and the addition of hydrochloric acid were studied. *A. niger* culture filtrate solubilized metals from the converter slag at levels of 18.70% copper, 7.40% nickel and 4.00% cobalt. Addition of hydrochloric acid was found to improve copper, nickel and cobalt solubilization to 46.52, 27.90 and 37.96%, respectively. HPLC analysis of the fungal culture filtrate revealed the presence of succinic and citric acids. Therefore, leaching of the slag was also carried out with matching concentrations of these organic acids individually as well as with both mixed together. Results are discussed.

Keywords: *Aspergillus niger*, bioleaching, citric acid, converter slag, succinic acid

Introduction

During the process of copper extraction the impurities come out as slag. About 18 000 tonnes of converter slag are produced annually at the copper smelter of M/s Hindustan Copper Ltd, Ghatshila (Bihar, India) alone (Sukla *et al.* 1986). This converter slag is, however, recycled to recover copper and, partially, nickel for considerable return of metal values as well as to reduce India's dependance on imported metals. Cobalt is not recovered and remains in the slag. The limited reserve of these metals and their high cost in the market requires the development of a relatively less expensive process for their recovery from slag. Copper, nickel and cobalt values worth more than Rs 9 crores can be obtained annually from this slag, thereby saving the country's foreign exchange. Copper is present in the converter slag as sulfides and oxides which can be leached out by microbial means.

Both chemolithotrophic and heterotrophic microorganisms play important roles in the solubilization of metal ions (Groudev *et al.* 1978, Trudinger *et al.* 1980, Ehrlich 1981, Torma 1981, Krumbein 1983). Heterotrophic bacteria and fungi are known to produce organic acids which can dissolve metals by forming salts or complexes like chelates (Berry *et al.* 1963, Ehrlich 1981). These chelates are soluble or insoluble depending on the structures of ligands and the relative stability of the complexes in relation to the E_h and pH of the system (Manskaya & Drosdova 1968). Fungi are well known for their ability to produce organic acids (oxalic, isocitric, succinic, maleic, citric acids, etc.) and, among them, *Aspergillus niger* has been most intensively studied (Henderson & Duff 1963, Chmiel 1976, Berry *et al.* 1977). The authors are not aware of any reports on the bioleaching of copper converter slag.

The aim of the present investigation was to leach the copper converter slag using *A. niger* culture filtrate.

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Materials and methods

Copper converter slag was collected from Ghatshila copper plant (Bihar, India). X-ray crystallographic analysis showed that the slag contained CuO, Cu_2O, Fe_3O_4 and Fe_2SiO_4 phases. Elemental analysis of the slag was performed using atomic absorption spectrophotometry. The slag was initially ground to $-150\ \mu m$ for leaching experiments.

Microorganisms

The *A. niger* strain used in the present investigation was obtained from Dr S. Groudev, Higher Institute of Mining and Geology, Bulgaria, and cultured in liquid medium containing (g/l): sucrose 100.00, NH_4Cl 1.50, KH_2PO_4 0.10, $MgSO_4 \cdot 7H_2O$ 0.80 and methanol 3%. The pH was adjusted to 6.50 and the medium was sterilized by autoclaving. Growth was carried out in a 500 ml conical flask containing 150 ml of medium. The incubation was done at 35 ± 1 °C for 4–5 days until the surface of the medium was completely covered with fungal mycelium in the form of a mat.

The culture filtrate was analyzed by HPLC (Model B-2830, Spectra Physics). An ultrasphere ODS column (150 × 4.6 mm inside diameter with 5 μm particles) preceded by a 50 × 4.6 mm guard column filled with 30–35 μm C_{18} reversed-phase packing was used for separation. The mobile phase used was a methanol–water mixture at 25 ± 1 °C with a flow rate of 30 ml h^{-1}. Prestabilization of the column was done with a methanol–water mixture. Solvent A was triple distilled water and solvent B was methanol (HPLC grade). The methanol percentage was varied from 30 to 90% to obtain better resolution of the intermediate acids of the citric acid cycle. A varian 8500 liquid chromatograph with a syringe pump connected to the detector and a recorder were used. Sample injection was performed by a stop flow technique. For the 'standard' run HPLC grade standards of oxalic, succinic and citric acids were used. Experimental culture filtrate was injected along with standard acid solutions.

Shake flask leaching experiments were carried out in 500 ml stoppered conical flasks containing 5 g of copper converter slag (−150 mesh) and 100 ml of culture filtrate. The flasks were agitated on a rotary shaker at 120 r.p.m. The effects of different leaching times, pulp densities and the addition of hydrochloric acid were studied to optimize recovery of copper, nickel and cobalt. A control experiment was run with sterilized distilled water.

Chemical leaching

Shake flask leaching experiments using citric, succinic and hydrochloric acid were carried out in order to compare the results of chemical leaching and bioleaching.

Metal analysis

Samples of 5 ml were collected from the flask during the course of the experiment (the volume was replaced by sterilized media). Samples were filtered and centrifuged at 10000 × *g* for 10 min in order to remove any microbial biomass present. The supernatant was then analyzed for cobalt, copper, nickel and iron by atomic absorption spectrophotometry (Perkin Elmer Model 1475) after proper dilution with distilled water.

Results and discussion

The chemical analysis results are given in Table 1. The percentages of copper, nickel and cobalt in the slag were found to be 4.03, 1.98 and 0.48%, respectively.

The optimum leaching time necessary for extracting metals was determined at 5% pulp density, pH 3.50, E_h = 240 mV and 30 °C. It was observed that maximum solubilization for copper, nickel and cobalt occurred within 48 h and further incubation did not substantially increase the extraction state of metals from the slag (Table 2). The percentage recovery for copper was more than that of cobalt and nickel.

The variation in the extraction of metal values by changing the pulp density from 1 to 5% while keeping the other parameters constant is shown in Figure 1. The decrease in the metal extraction values with an increase in pulp density indicates that the organic acid produced by *A. niger* may not be available in sufficient amounts to extract metals from the substrate. The decrease in the recovery of

Table 1. Elemental analysis of copper converter slag

Element	Percentage
Cu	4.03
Ni	1.98
Co	0.48
Fe	38.82
Ca	4.01
Mg	2.65
Al	0.08
SiO_2	34.32

Table 2. Effect of incubation time on the leaching of copper converter slag with *A. niger* culture filtrate at 5% pulp density and 30 °C temperature

Duration of leaching (days)	Final pH	Percent recovery			
		Cu	Ni	Co	Fe
24	5.75	11.60	2.96	0.52	0.182
48	5.75	12.08	3.67	0.62	0.185
72	5.80	12.08	3.67	0.62	0.189
96	5.80	12.08	3.67	0.62	0.192
120	5.90	12.08	3.67	0.62	0.195

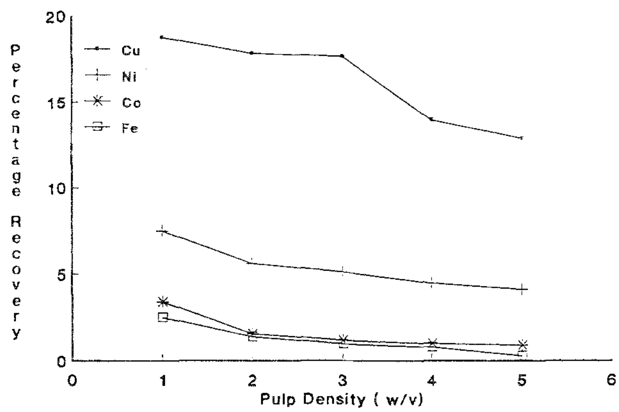

Figure 1. Effects of different pulp densities of copper converter slag on the percentage recovery of copper, nickel, cobalt and iron after leaching with *A. niger* culture filtrate.

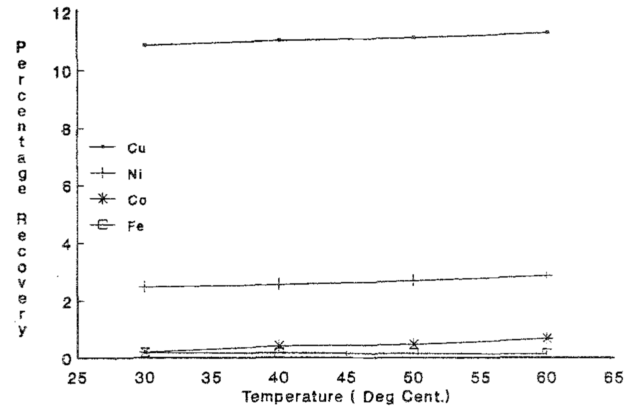

Figure 2. Effects of leaching temperature on the percentage recoveries of copper, nickel, cobalt and iron from copper converter slag leached with *A. niger* culture filtrate.

all four metals at higher pulp density tested might also be due to the combined effect of the high viscosity of the slurry and less dissolved oxygen.

The percentage recoveries for different metals at leaching temperatures ranging from 30 to 60 °C are shown in Figure 2. The increase in the recovery of metals with increasing leaching temperature was not found to be significant.

The recovery of metal values was increased by the addition of hydrochloric acid to the culture filtrate, which decreased the pH values of the leachate to 3.50. Percentage recoveries of copper, nickel, cobalt and iron with the addition of different quantities of hydrochloric acid (0.5–2.0 ml) are shown in Figure 3. Addition of hydrochloric acid to culture filtrates improved copper, nickel, cobalt and iron recoveries significantly. The increase was maximum for cobalt and minimum for copper.

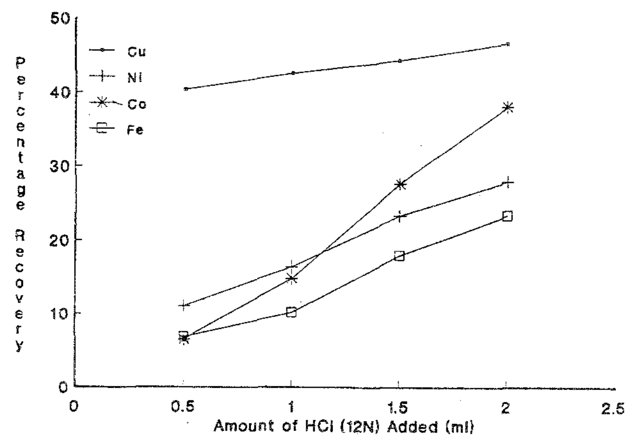

Figure 3. Effects of addition of different quantities of hydrochloric acid on the leaching of copper converter slag with *A. niger* culture filtrate.

The HPLC results showed the presence of succinic and citric acid in the *A. niger* culture filtrate at concentrations of 11.37 and 10.02% (0.52 M), respectively. Therefore, the same concentration of succinic acid and citric acid was taken for leaching the slag separately. In another experiment both the organic acids were mixed in the same concentrations and leaching was carried out. A 5% pulp density and a leaching time of 4 h were used in all these leachings. Table 3 summarizes the results of the above experiments.

Table 3. Chemical leaching of copper converter slag (4 h at 5% pulp density)

Leaching agents used	Percent recoveries			
	Cu	Ni	Co	Fe
Distilled water	6.7	–	–	–
Succinic acid	17.0	4.87	4.0	1.20
Citric acid	23.0	4.00	5.70	1.50
2% HCl	32.11	13.23	14.04	20.29
Mixture of acids	46.52	7.90	9.60	23.0

The above investigations have shown that the culture filtrate of *A. niger* can dissolve copper, nickel, cobalt and iron from copper converter slag. The addition of hydrochloric acid caused an enhancement in the recoveries of these metals. The H^+ ion of hydrochloric acid possibly attacks the mineral matter and the organic acids chelate the metals. Therefore, along with organic acids present in the culture filtrate (produced as a result of *A. niger* growth), addition of hydrochloric acid is also needed to enhance the leaching of metals present.

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