APPENDIX

(PAPERS PUBLISHED/PRESENTED)

Removal of sulfur from Assam coal by bacterial conditioning and froth flotation

Celin Acharya,[1] Gedela V Rao,[1] Irena Twardoska,[2] Rabi N Kar[1] and Lala B Sukla[1]*

[1]Regional Research Laboratory, Bhubaneswar-751 013, Orissa, India
[2]Institute of Environmental Engineering, Polish Academy of Sciences, Poland

Abstract: Reduction of sulfur by bacterial leaching from a high sulfur-bearing coal sample from Assam was attempted. Flotation of the sample with light diesel oil could not depress the pyrite and also the *Thiobacillus ferrooxidans* was found to be ineffective in leaching the sulfur from the flotation concentrate. Conditioning of the same coal sample with *Thiobacillus ferrooxidans* was found to assist in selectively depressing the pyrite, thereby reducing nearly 60% of the pyritic sulfur present in the sample.

Keywords: *Thiobacillus ferrooxidans*; coal; sulfur; bacterial conditioning; froth flotation

1 INTRODUCTION

The high sulfur content of coals in North Eastern India imposes severe limitations on their utilisation as the sulfur oxide gases evolved from the combustion of coal result in acid rains. Therefore, removal of sulfur is essential before combustion of the coal. There are several physical, chemical and biochemical techniques for removing or reducing the sulfur content of the coal before combustion. Among these physical and chemical techniques, froth flotation is one of the most efficient processes for pyrite removal from high sulfur coal.[1,2] However, pyrite separation from high sulfur coals is often inadequate using the standard flotation process. Vaaler and Attia suggested that if selective modification of the surface chemical and flotation behaviours of pyrite could be achieved by biological conditioning using sulfur-oxidising bacteria like *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*, the separation of pyrite from coal by flotation might be possible.[3] The major part of inorganic sulfur in coal consists of pyrite (FeS_2), which occurs in particulate form, or sometimes agglomerated into balls or nodules, but usually it is very finely disseminated.[4] Many reports have shown that *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* have been quite successful in decreasing pyritic sulfur, though not so successful in removing organic sulfur.[5–7] Pyrite has been identified both macroscopically and microscopically in coals from Assam.[8] The overall reaction for microbial pyrite oxidation is:

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (1)$$

The effect of chemical pretreatment on bacterial desulfurisation of Assam coal has been studied.[9] Microorganisms have been used to depress the pyrite during froth flotation of coal by altering the surface properties. The bacterial pre-conditioning of coal before flotation was reported to modify the surfaces of pyrite particles and assist its depression into the tailings during flotation.[10]

In this paper, attempts made to reduce sulfur from high sulfur-bearing coal from Assam by bacterial conditioning with *Thiobacillus ferrooxidans* followed by flotation are discussed along with the characterisation aspects of flotation tailings.

2 SAMPLES AND CHARACTERISATION

2.1 Coal

A high sulfur-bearing coal sample obtained from the North Eastern Coalfields of Tinsukia district, Assam, was used in this work. Moisture, volatile matter, fixed carbon and ash content of coal sample were analysed (Table 1). The sample was roll-crushed and classified into various size fractions. All the fractions were analysed for pyritic and organic sulfur as per standard methods and the compositions are given in Table 2.[11] For the purpose of this work, the sample was ground to 100% passing 75 μm size.

2.2 Bacterial strain

A laboratory stock culture of *Thiobacillus ferrooxidans*, previously isolated from Amjhore pyritic mine water,[12] was used in this experiment. It was grown in mineral salt medium containing (dm^{-3}): $MgSO_4.7H_2O$, 0.5; KH_2PO_4 0.5; $(NH_4)_2SO_4$, 3.0; KCl, 0.1; $FeSO_4$,

* Correspondence to: Lala B Sukla, Regional Research Laboratory, Bhubaneswar-751 013, Orissa, India
E-mail: root@csrrlbhu.ren.nic.in
Contract/grant sponsor: CSIR
(Received 24 November 1998; revised version received 21 April 1999; accepted 18 May 1999)

Table 1. Proximate analysis of various size fractions of coal

		Constituents (%)				Distribution (%)			
Size μm	Wt (%)	Moisture	Volatile matter	Ash	Fixed carbon	Moisture	Volatile matter	Ash	Fixed carbon
−210+150	59.8	2.10	39.3	3.60	55.0	57.0	60.3	55.4	59.9
−150+75	14.4	2.10	39.0	3.20	55.7	13.7	14.4	11.8	14.6
−75+45	10.4	2.20	39.0	3.60	55.2	10.4	10.4	9.64	10.4
−45	15.4	2.70	37.8	5.00	53.7	18.9	14.9	19.8	15.1
Calc (Head)	100	2.20	38.94	3.88	54.9				

Calc (Head): Cumulative assay obtained by multiplying wt% of each size fraction with the assay % of corresponding constituent.

Table 2. Analysis of sulfur in various size fractions of coal

		Sulfur (%)			Distribution (%)		
Size (μm)	Wt (%)	Pyritic	Organic sulfate	Total	Pyritic sulfate	Organic sulfate	Total sulfur
−210+150	59.8	1.46	3.94	5.40	58.1	60.9	60.1
−150+75	14.4	1.96	2.71	4.67	20.1	10.8	13.4
−75+45	10.4	1.36	3.83	5.19	9.0	10.3	10.0
−45	15.4	1.29	4.83	6.12	12.4	18.0	16.4
Calc (Head)	100	1.50	3.867	5.369	100		

Calc (Head): Cumulative assay obtained by multiplying wt% of each size fraction with the assay % of corresponding constituent.

Table 3. Analysis of raw coal, coal after conditioning (feed), tailings and concentrate (in %)

	Wt	Iron	Total S	Moisture	Volatile matter	Ash	Fixed carbon
Concentrate	97 8	0.71	5.17	2.7	38	4.94	56.20
Tailings	2 20	51.6	34.54	2.5	1.00	63.60	1.8
Feed (after conditioning)	100	1.845	5.91	2.3	38.5	5.94	55.58
Raw coal	—	1.54	6.74	2.2	39.00	5.85	55.9

44.2; pH 2.5 adjusted with 2 mol dm^{-3} sulfuric acid. It was activated and later adapted to finely ground ~75 μm diameter) coal.

3 EXPERIMENTAL

3.1 Bacterial culture technique

3.1.1 Activation

A sample from stored laboratory stock culture of *Thiobacillus ferrooxidans* was used for activation. Ten cm^3 of stored bacterial culture, 20 cm^3 of mineral salt medium with 20 cm^3 of distilled water were taken in sterilised 250 cm^3 Erlenmeyer flasks. The pH value was adjusted to 2.5 with 2 mol dm^{-3} sulfuric acid. The bacteria were incubated at 30 °C under shaking conditions (140 strokes min^{-1}). Activation was achieved by three successive re-inoculations at weekly intervals.

3.1.2 Adaptation

Activated cultures of *Thiobacillus ferrooxidans* were used for preparation of adapted cultures on ground coal. The analyses of the coal sample used for bacterial adaptation, pre-conditioning and flotation is given in Table 3. For adaptation, four 500 cm^3 flasks, each containing 60 cm^3 activated culture, 2–8 g of 75 μm coal and 200 cm^3 distilled water were used. The pH was adjusted to 2.5 in each case with dilute H_2SO_4. Bacteria were adpated to increasing concentrations of coal (2–8 g) by weekly transfers over four successive weeks. Subsequently, the flask content was filtered using Whatman filter paper No 541 and the filtrate was used for bacterial pre-conditioning.

3.1.3 Pre-conditioning

A 200 cm^3 aliquot of adapted culture solution (3.32×10^9 cells cm^{-3}) was added to 50 g of the ground coal, the pH adjusted to 2.0 and the culture incubated at 30 °C with shaking for 5 days. Subsequently, the bacterial suspension was filtered using Whatman filter paper No 541, the residual coal washed with distilled water, dried, analysed, and used for froth flotation.

3.2 Froth flotation studies

Flotation experiments were performed with a Denver D-12 sub-aeration flotation cell at 1500 rpm using tap water of pH 5.8. Initially flotation experiments were carried out on the ground sample. Around 40 g of sample was conditioned with 4 kg $tonne^{-1}$ light diesel

Table 4. Analyses of flotation products

		Assay (%)		Distribution (%)	
Flotation products	*Wt (%)*	*S*	*Fe*	*S*	*Fe*
Concentrate	97.1	5.90	0.95	97.9	73.0
Tailings	2.9	4.36	11.75	2.1	27.0
Calc (Head)	100	5.855	1.26	100	100

Calc (Head): Wt% of conc x assay % + wt of tailings x assay %.

oil at 10% (w/v) solids and coal was floated at 30 ppm MIBC (methyl iso-butyl carbinol).

The concentrate and tailings were collected, dried, weighed and analysed for both pyritic sulfur and total sulfur (Table 4). Flotation studies were also carried out on the sample conditioned with the mesophilic bacterium *Thiobacillus ferrooxidans*. A bacterial pre-conditioned coal sample of around 40 g was treated with 2 g kg^{-1} light diesel oil and 30 ppm MIBC and floated the material at neutral pH. The concentration and tailing samples were dried, weighed and analysed for fixed carbon, volatile matter, ash, pyritic sulfur and organic sulfur contents (Table 3).

4 CHARACTERISATION OF FLOTATION TAILINGS

4.1 XRD Analysis

A flotation tailing sample obtained on bacterial-conditioned material was analysed by Philips XR Diffractometer (PW 1710, PW 1830 and PW 1820) equipped with Cu K_α-radiation and a wide range goniometer having a diffracted beam monochromator and Q compensating slit (Fig 1).

4.2 Microscopic studies

A polished section of tailing sample was prepared as per standard procedure (IS9217) and was observed under Leitz reflected high metalloplan microscope by means of dry objectives (Fig 2).

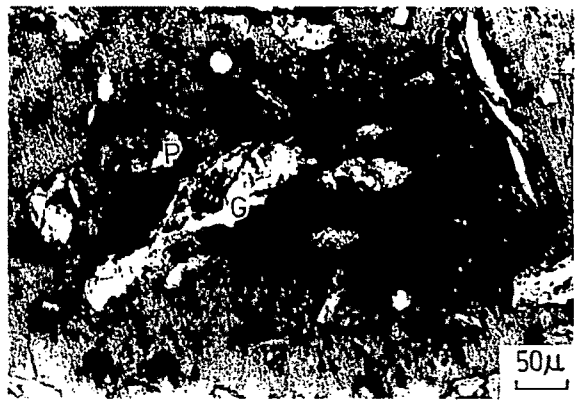


Figure 2. Photomicrograph of the flotation tailings of Assam coal showing the presence of goethite (G), haematite (H), pyrite (P) and silicate (dark grey): reflected light.

5 RESULTS AND DISCUSSION

The coal sample having 56% (w/w) fixed carbon and 39% (w/w) volatile matter had around 5.4% (w/w) total sulfur with 28% (w/w) of it as pyritic sulfur (Table 1). Table 2 shows that both pyritic and organic sulfur are more or less consistent in all the size fractions of the sample. Flotation results on the sample indicated (Table 4) that only around 27% of the iron present in the sample could be rejected in the tailing, while 98% of the sulfur was in the concentrate. This indicates the iron reported as gangue in the tailings may be predominantly goethite since the sulfur content in the tailing was 4.36%.

From Table 3, it was observed that the iron content increased marginally from 1.54% in the raw coal to 1.84% in the feed obtained after bacterial condition-

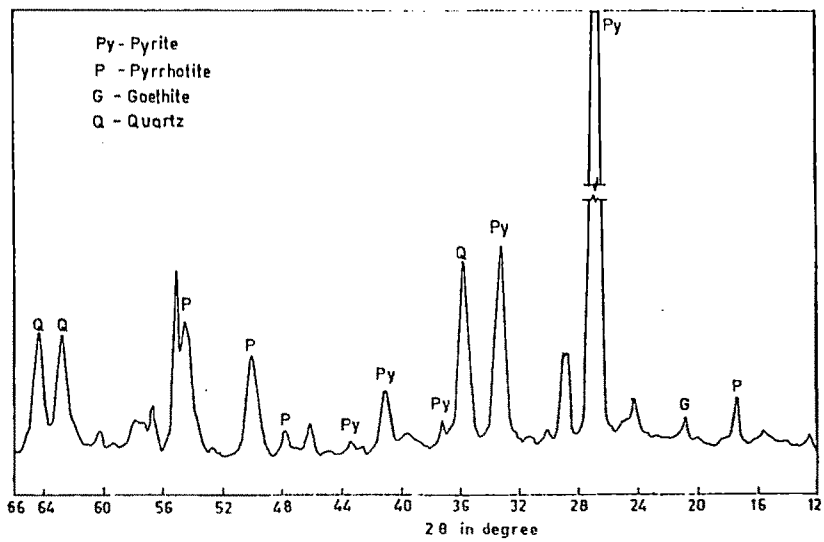


Figure 1. X-ray diffractogram of tailings sample.

ing, this was due to the formation of jarosites during bacterial growth according to the following reaction.[13]

$$3Fe^{3+} + M^{+} + 6H_2O + 2H_2O + 2SO_4^{2-} \longrightarrow MFe_3(SO_4)_2(OH)_6 + 6H^{+}$$

where M^{+} may be potassium or hydrogen. After flotation, the iron content in the coal concentrate was found to be only 0.71%, indicating the removal of a major portion of iron through this method. The iron content of 51.6% Fe in the tailings along with 35% S indicates the possible presence of pyrite.

The XRD data (Fig 1) on the flotation tailings confirmed the iron as pyrite and also indicated the presence of goethite. The mineralogical data (Fig 2) also confirmed the iron present in the tailings as pyrite and goethite. A decrease in total sulfur in the feed (around 12.3%) can be observed from Table 3. It may be due to the fact that the microorganism has a higher affinity for sulfur than for iron. A total of 23.2% of the sulfur has been removed from the coal sample by bacterial conditioning followed by flotation.

The adaptation period of *T ferrooxidans* on the pyrite substrate prior to bacterial pre-conditioning has a positive effect on pyrite rejection. This may be due to the fact that the longer adaptation period leads to development of bacterial cultures tolerant to the pyrite suspension environment. These cultures produce more surface active substances which are selectively adsorbed on the pyritic surfaces of the coal, making them more hydrophilic and leading to pyrite depression.[14] In view of these findings it can be concluded that bacterial pre-conditioning with *Thiobacillus ferrooxidans* before froth flotation has a significant effect on pyrite removal in particular and total sulfur removal in general.

6 CONCLUSION

(1) Bacterial pre-conditioning with adapted cultures of *Thiobacillus ferrooxidans* on pyrite substrate, ie, coal, followed by froth flotation process has a significant positive effect on sulfur removal from a high sulfur-bearing coal from Assam.
(2) Around 23.2% of total sulfur could be removed from the coal sample using this technique.
(3) The adaptation period of *Thiobacillus ferrooxidans* on pyrite substrate or coal before conditioning plays a positive role in the removal of sulfur from the coal sample.
(4) By this process, the quality of coal from Assam is improved due to removal of sulfur, as well as a reduction in ash content.

ACKNOWLEDGEMENTS

The authors are thankful to Dr HS Ray, Director and Dr RP Das, Deputy Director and Head, Hydro & Electrometallurgy Division, RRL Bhubaneswar for providing facilities for the work. Coal samples were provided by Mr MC Bora, Area Manager, North Eastern Coal Fields, Assam. The authors wish to thank Dr BS Acharya and Dr BC Acharya for their help in XRD and microscopic studies respectively. The first author, CA, thanks CSIR for granting a Senior Research Fellowship.

REFERENCES

1 Miller KJ and Baker AF. *Flotation of Pyrite from Coal,* Bureau of Mines. US Dept of Interior Tech Report, pp 51 (1992).
2 Wheelock TD and Ho TK. Modification of the flotability of coal pytrite, in *AIME Annual Meeting.* New Orleans. Louisiana. pp 18–22 (1979).
3 Attia YA and El Zeky M. Coal slurries desulphurisation by flotation using thiophilic bacteria for pyrite depressions. *Coal Slurry Fuels Prep Util Proc Int Symp* 8:242–261 (1986).
4 Couch GR. *Biotechnology and Coal.* Report ICTIS TR 38. IEA Coal Research London (1987).
5 Kargi F.Microbiological coal desulphurization. *Enz Microbiol Technol* 13–19 (1982).
6 Dugan PR and Apel WA. *Microbial Desulphurisation of Coal, Metallurgical Applications of Bacterial Leaching and Related Phenomena,* Ed by Murr LE Torma AE and Brierley JA. Academic Press. New York. pp 223–250 (1978).
7 Acharya C, Kar RN, Twardoska I, Sukla LB and Mishra SK. Microbial desulphurisation of Assam Coal. *Indian J of Microbiol* 37:17–20 (1997).
8 Chaudhury SG, Ghose S and Chandra D. Origin and mode of occurrence of pyrite in Assam coal. *Fuel Sci and Technol* 1:41–46 (1982).
9 Tripathy SS, Kar RN, Mishra SK, Twardoska I and Sukla LB. Effect of chemical pretreatment on bacterial desulphurisation of Assam coal *Fuel* 8:859–864 (1998).
10 Attia YA and El Zeky M. Biosurface modification in the separation of pyrite from coal by froth flotation, in *Proc of the First Int Conf on Processing and Utilization of High Sulfur Coals* October 13–17. Columbus, Ohio, USA. Ed by Attia YA, pp 673–682 (1985).
11 IS, Indian Standard Methods of test for coal and coke. 1350 (1969).
12 Kar RN, Chaudhury GR, Sukla LB and Das RP. Kinetics of iron oxidation as well as precipitation by *Thiobacillus ferrooxidans* in presence and absence of various metal ions. *Enzmetall* 44:212–215 (1991).
13 Murr LE and Mehta AP. Coal desulphurization by leaching involving acidophilic and thermophilic microorganisms. *Biotechnol Bioeng* 24:743–748 (1982).
14 Kepton AG, Moneib N, McCready RGL and Capes CE. Removal of pyrite from coal by conditioning with *Thiobacillus ferrooxidans* followed by oil agglomeration *Hydromet* 5:117–125 (1980).

Indian Journal of Microbiology, Vol 37 March 1997, pp 21-24

Microbial Depyritization of Assam Coal

C Acharya, RN Kar, SK Mishra, I Twardoska[1] and LB Sukla*
Division of Hydro and Electrometallurgy, Regional Research Laboratory, CSIR, Bhubaneswar - 751 013, **India.**
[1]Institute of Environmental Engineering, Polish Academy of Sciences, **Poland.**

Laboratory studies were conducted using Assam coal to determine the removal of pyritic sulphur by *Thiobacillus ferrooxidans* and the factors that may limit the microbial depyritization. Leaching experiments were conducted using different size fraction of coal samples. Removal of pyrite was monitored by analysis of soluble iron in the leachate. Little precipitation of jarosite occurred during leaching. Soluble iron in the leachate was predominantly Fe(III). *Thiobacillus ferrooxidans* removed around 30% pyrite. It catalyzed pyrite dissolution by a mechanism which involved bacterial oxidation of ferrous iron in solution. Results suggest that the ferric iron was predominantly leached from the coal. It also indicated that direct contact of the bacterium was essential in pyrite oxidation.

Key words: *Thiobacillus ferrooxidans*, Assam coal, depyritization, pyrite

Coal, an abundant source of energy, is becoming costly day by day and therefore, certain technological processes have gained considerable interest in developing country, including India. In North-Eastern region of India, the coal being used, contain high levels of sulphur which is causing threat to environment. The greatest pollution threat is because of the formation of sulphur dioxide which together with oxides of nitrogen causes acid rains.

Removal of pyritic sulphur from coal using microorganisms was first reported by Silverman *et al.* (1). Methods of microbial desulphurisation of coal have been extensively studied during the past decade. The bacterium *Thiobacillus ferrooxidans* is known to remove pyrite from coal upto 90% (2). Assam coal contains all forms of pyrite of which framboidal type is highly susceptible to oxidation. This type of pyrite is one of the main constituents influencing the acidic nature of the mine water (3). It is difficult to remove the finely disseminated pyrite in coal by conventional physical cleaning processes. It can be removed through microbial desulphurisation prior to combustion. Adapted bacteria have been shown to remove 80% pyritic sulphur from coal (4). Kinetic analysis performed by Olsson *et al.* (5) have shown the first order reaction in microbial oxidation of pyrite. Pyrite particles exposed on the outer surface of the coal might be subjected to microbial attack directly, where as, pyrite crystals embedded in the coal structure can probably be attacked by ferric ions as in chemical leaching (6).

The contact between coal surface and bacteria is necessary as addition of surfactants to growth medium is known to enhance desulphurisation (7). The sulphur in pyrite is present as S_2^{2-} and the S atoms migrate to the pyrite surface by molecular diffusion. The jarosite precipitation is the indication of Fe^{2+} oxidation in coal. Eligwe (8) suggested oxidation of pyrite by direct as well as indirect mechanisms. In the direct oxidation physical contact of microbial cells is essential while in indirect mechanism pyrite is oxidized chemically by ferric ions produced from microbial activity. In the present study, the effect of different parameters like pH, pulp density and particle size on pyrite removal from coal were examined.

*Corresponding author

Materials and Methods

Coal sample: Coal samples were obtained from North - Eastern coal fields, Tinsukia District, Assam. The samples were crushed finely and sieved through different pore size sieves. Different particle size fractions were analyzed for pyritic sulphur, sulphate sulphur, organic sulphur and total sulphur as per standard methods(9). Moisture content was determined by drying samples in an oven at 104^0 C constantly for 12 h. The samples were then kept in muffle furnace at 700^0 C to determine ash content. Metal content was estimated by atomic absorption spectrophotometric analysis of acid digested coal samples.

Bacterial strain: Thiobacillus ferrooxidans was obtained from Dr. KA Natrajan, Department of Metallurgical Engineering, I.I.Sc., Bangalore. The bacterium was grown in mineral salt medium containing (g l^{-1}): $MgSO_4$. $7H_2O$, 0.5; K_2HPO_4, 0.5; $(NH_4)_2SO_4$, 3.0; KCl, 0.1; $FeSO_4$, 44.2; pH , 2.5 adjusted with sulphuric acid.

Experimental procedure: The experiments were conducted in 250 ml conical flasks containing 90 ml broth added with known amount of coal. The medium was sterilized by autoclaving and inoculated with 10 ml of culture broth of *T. ferrooxidans* cell suspension (10^6 cells ml^{-1}). The flasks were incubated at 30 ± 2^0 C. Samples were withdrawn at regular intervals and analyzed for iron. The influence of different parameters

on pyrite oxidation was studied for 15 to 35 d. The parameters were: (i) Effect of initial pH (1.5 to 3.0) with 1% coal having 72-100 BSS particles, on leaching up to 15 d of incubation, (ii) Effect of pulp density with 2 and 4% coal (300-350 BSS) and (iii) Effect of coal particle size with 1% coal having particle size ranging from 100 to 350 BSS with initial pH of 2.5 and Eh 340-350 mV. Suitable uninoculated controls were kept in each case.

Results and Discussion

The amount of different types of sulphur present in various size fractions of Assam Coal is presented in Table 1. Quantities of different types of sulphur varied with the mesh size, the organic sulphur being in higher concentration in all size particles and the inorganic being at minimum.

Table 1. Sulphur content in different particle size fractions.

Type of Sulphur	Particle size (BSS)			
	72-100	100-200	200-300	300-350
Total Sulphur	5.50	6.12	5.21	3.92
Pyritic sulphur	1.46	1.29	1.36	1.96
Organic sulphur	3.87	4.74	3.76	1.88
Sulphate sulphur	0.17	0.09	0.09	0.08

Effect of initial pH: Reduction in the pH of the leaching medium was observed as the leaching proceeded. An initial optimum pH was observed to be in the range of 2.5 to 3.0 (Table 2). The acidity increased and the pH lowered in all the cases but pyrite conversion was maximum in samples having initial pH of 2.5.

Table 2. Effect of initial pH on pyrite oxidation by *T. ferrooxidans.*

Initial pH	Initial Eh	Final pH	Final Eh	% Pyrite conversion
1.5	410	1.3	670	17.96
2.0	410	1.8	650	18.24
2.5	420	1.9	650	24.29
3.0	420	2.2	610	19.39

The reduction at pH 3 was mainly due to precipitation of jarosites. *T. ferrooxidans* oxidizes both the ferrous and the sulfide moieties of pyrite. The sulfide oxidation produces sulphuric acid more than required for oxidation of ferrous part. As such pyrite oxidation reduce the pH and the rate of oxidation was negligible below pH 1.5. It shows that increase in acidity is a rate limiting factor for bacterial pyrite oxidation. Similar observations were made earlier (10). Increase in initial pH has been shown to stimulate jarosite formation (11) which prevent subsequent oxidation by bacteria and decrease pyrite leaching.

Influence of pulp density: There was a negative effect on pyrite oxidation with increase in pulp density (Table 3). The conversion was better at 2% pulp density as compared to conversion at 4%. The drop in pH was upto 1.7 at 2% and to 1.6 at 4% of pulp density. The redox potential also differed at the end of 18 d of incubation. Bacterial oxidation increased redox potential of the medium, resulting into oxidative environment. With increase in pulp density, resulting in decrease in pyrite, could be due to limitation in other nutrients, reduced oxygen availability or due to attrition of cells with solids at high pulp density. The representative solution for ferrous and ferric iron was analyzed at the end of leaching process. It was observed that the solution contained 90% ferric and 10% ferrous iron indicating that most of the Fe^{2+} was oxidized to Fe^{3+} by the bacteria.

Table 3. Effect of pulp density on Eh, pH and pyrite conversion from coal by *T. ferrooxidans* (particle size 300-350 BSS).

Incubation period (d)	Pulp density (%)					
	2			4		
	pH	Eh	% Pyrite oxidation	pH	Eh	% Pyrite oxidation
0	2.5	350	0.0	2.5	350	0.0
3	2.2	425	1.4	2.1	475	1.0
6	2.0	550	5.4	1.9	550	3.6
9	1.8	575	14.6	1.7	550	9.4
12	1.7	650	17.6	1.6	635	12.8
15	1.7	660	17.6	1.6	640	15.6
18	1.7	675	17.8	1.6	640	16.0

Effect of particle size: The effect of coal particle size on pyrite oxidation is depicted in Fig. 1. Oxidation rate was faster and better quantitatively in sample having fine particles (300-350 BSS) as seen from the slope of the curves. However, after 15 d of incubation there was no further oxidation and the values remained static upto 35 d. In bacteria free control sample, the conversion was negligible.

Effect on ash after bacterial oxidation: The ash content was determined after 25 d of bacterial oxidation (Table 4). Although there were minor variations in the initial ash content in different size fractions, the % reduction in ash after bacterial oxidation was maximum in finer particle

coal (300-350 BSS). This was probably due to removal of dissolved metal ions in the leachate after bacterial oxidation of pyrite which resulted in lowering of pH.

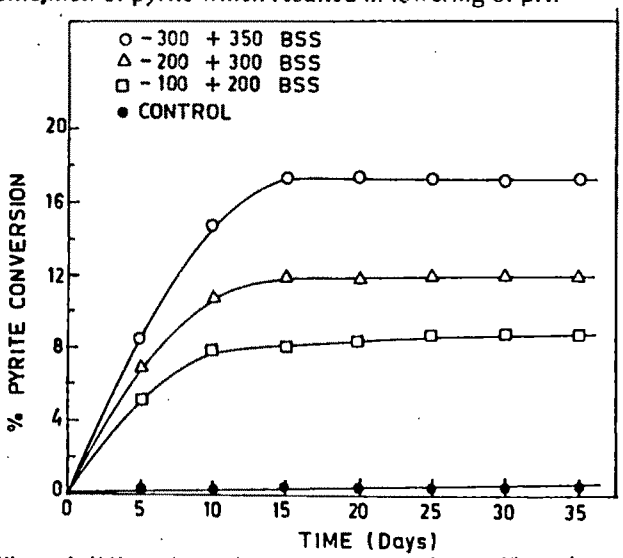


Figure 1. Effect of particle size on pyrite oxidation (1% coal).

Table 4. Ash content of coal after bacterial leaching for 25 d.

Particle size (BSS)	Ash content (%)		
	Initial	Final	% Reduction
72-100	3.60	2.45	31.90
100-200	3.20	1.95	38.70
200-300	3.60	2.15	40.20
300-350	5.80	3.76	35.17

Metal leaching during pyrite oxidation: The analysis of different particle size coal, after bacterial oxidation and leaching, showed removal of other cations like Ni, Co. Mn and Cr (Table 5).The leaching of these metal ions also varied with particle size. Maximum leaching for these cations was observed in particles of 100-200 BSS. The removal of these heavy metals along with ferric sulphate is advantageous as it lead to reduction of these metals in fly ash.

Kinetics: The kinetics of the reaction was controlled by chemical oxidation of pyrite by ferric iron and the following rate equation was applicable in the present case: $1-(1-F)^{1/3} = kt$, (F- fraction reacted)

where $1-F = R$ (residual pyrite fraction)

$-R^{1/3} = -1+kt$ or $R^{1/3} = 1-kt$

Since the plot of $R^{1/3}$ vs. time (t) gives a straight line (Fig. 2), the reaction is chemically controlled. That a surface electrochemical reaction controls leaching, is suggested by a linear relationship between the rate constant k and 1/r where r is the particle radius (Fig. 3).

Table 5. Bioleaching of heavy metals from coal (25 d).

Particle size (BSS)	Metal content (%)		
	Initial	Final	% Removal
	Nickel		
72-100	0.0230	0.0181	21.3
100-200	0.0162	0.0103	36.4
200-300	0.0197	0.0137	29.9
300-350	0.0260	0.0160	36.9
	Cobalt		
72-100	0.0065	0.0045	29.2
100-200	0.0135	0.0111	17.7
200-300	0.1325	0.1025	22.5
300-350	0.0255	0.0230	9.4
	Manganese		
72-100	0.0180	0.0135	25.0
100-200	0.0150	0.0035	76.0
200-300	0.0565	0.0171	69.5
300-350	0.0200	0.0150	23.0
	Chromium		
72-100	0.0140	0.0091	35.0
100-200	0.0727	0.0412	43.1
200-300	0.0130	0.0075	41.5
300-350	0.0160	0.0110	30.6

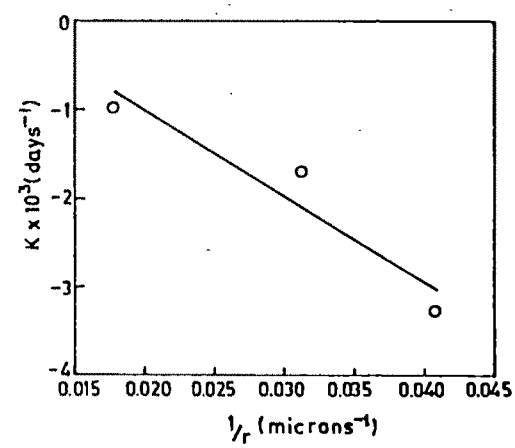


Figure 2. Kinetics of pyrite oxidation.

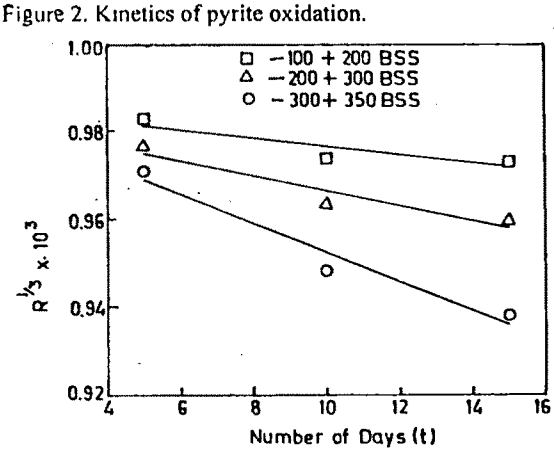


Figure 3. Rate constant for pyrite oxidation in relation to BSS.

The results in the present studies have demonstrated 25% removal of pyrite sulphur from Assam coal with particle size of 300-350 BSS and initial pH of 2.5. The microbial coal cleaning process, though not conventional as yet, holds great potential for the future.

Acknowledgments

The authors are thankful to Dr. HS Ray, Director and RP Das, Deputy Director, RRL, Bhubaneswar, for providing facilities. Coal samples were provided by Mr MC Bora, Area Manager, North Eastern Coal Fields, Assam.

References

1. **Silverman MP, Rogoft MH & Wender I,** *Fuel,* **42** (1963) 113.
2. **Cough GR,** *Report ICTIS TR 38,* IEA Coal Res. London (1987) 56.
3. **Chaudhuri SG, Ghose S & Chandra D,** *Fuel Sci Technol* **1** (1992) 41.
4. **Johanson DB & Rang L,** *J Gen Microbiol,* **139** (1993) 1417.
5. **Olsson G, Larsson L, Holst O & Karlson MT,** *Chem Engg Technol,* **16** (1993) 180.
6. **Hone HJ, Beyer M, Ebner HG, Klein J & Juntgen H,** *Chem Eng. Technol* **10** (1987) 173.
7. **Sand W,** *Env Technol Lett,* **6** (1985) 439.
8. **Eligwe CA,** *Fuel* **67** (1988) 451.
9. **IS** *Indian Standard Methods of Test for Coal & Coke,* (1969) 1350
10. **Roy P & Mishra AK,** *Indian J Expl Biol,* **19** (1981) 729.
11. **Bogdigian RM & Meyerson AS,** *Biotechnol Bioengg,* **24** (1986) 467.

Desulphurisation of Low Ash and High Sulphur Coal from Assam

C. Acharya*, G.V. Rao*, R.N. Kar*, & L.B. Sukla*

A coal sample from Assam containing 6.12% total sulphur, 1.5% iron, and 3 to 4% ash was subjected to flotation to reject the pyritic gangue as well as the associated sulphur.The flotation tailings although assayed 11.7% Fe,. most of it was goethitic iron and contained only 2% of the sulphur. The flotation concentrate containing 5.9% total sulphur and 0.95% Fe was bioleached in order to study the extent of sulphur reduction. It was ascertained that 15% of total sulphur can be removed by Pseudomonas aureofaciens from the flotation concentrate. However, Thiobacillus was ineffective in removing the sulphur from the flotation concentrate probably due to the presence of residual diesel oil coating, formed during flotation, on the surface of coal particles.

INTRODUCTION

The high sulphur content of many coals imposes severe limitations on their utilization. Sulphur dioxide gases emitted from combustion of coal are blamed for acid precipitation problem. Among the physical and chemical techniques, froth flotation is one of the most effective processes for pyrite removal from high sulphur coal[1,2]. Also sulphur removal from coals using biological techniques appears to offer an attractive possibility. Most of the work reported on microbial coal depyritization has used Thiobacillus ferrooxidans[3]. We have achieved around 30% pyrite removal from Assam coal using Thiobacillus ferrooxidans[4]. Organic sulphur is mainly present in coal as covalently bound thiol, mercaptan sulphide and thiopene groups. It has been found that diobenzothiopene degrading microorganisms like Pseudomonas aureofaciens[5] and Rhodococcus rhodochorus[6] are capable of removing organic sulphur from coal. Dogan et al., were able to reject pyrite from sub-bituminous coals in the range of 70 to 80% by the use of bacterial conditioning followed by flotation[7].

In this article, attempts made to reduce the sulphur from a low ash and high sulphur coal sample from Assam, by froth flotation followed by bacterial leaching of the flotation concentrate are highlighted and discussed.

EXPERIMENTAL

Materials

Coal sample

Coal sample was obtained from North Eastern Coal Fields, Tinsukia District, Assam. This coal sample was chosen particularly due to it's high sulphur content (5-6%). This sample contains around 55% fixed carbon, 39% volatile matter, 2.3% moisture, 1.5% Fe, 6.12% sulphur and 4% ash.

* Regional Research Laboratory, Bhubaneswar-751 013, Orissa, India.

Microorganisms. The experiments were carried out using three bacterial cultures-

- A mixed culture of Thiobacillus available in laboratory stock culture was used. It was grown in nutrient medium contain (g/l) : $(NH_4)2S0_4$ 0.2; KH_2P0_4 3.0; $MgS0_4.7H_20$ 0.5. $CaCl_2.6H_20$ 0.25; KCl 0. 1; $F_eSO_4.7H_20$ 22.4; SO 5. 0; pH 2. 5 adjusted with sulphuric acid.
- A Pseudomonas aureofaciens culture (NCIM 2026) was obtained form National. Chemical Laboratory, Pune. It was grown in nutrient medium containing (g/l) : $(NH4)_2S0_4$ 0.25; $MgS0_4.7H20$ 0.75; $Na_2SO_4.H_20$ 0.3; KH2P04 0.25. Yeast extract 1.0; Glucose 20.00; pH 7.0 adjusted with sulphuric acid.
- A pure culture of Rhodocucus rhodochrorus (MTCC 289) was obtained from IMTECH, Chandigarh. It was grown in basic salt medium containing (g/l) : KH_2P0_4 4.0; Na_2H P04.H_20 4.0; NH_4Cl_2 2.0; $MgCl_2.6H_20$ 0.2, $CaCl_2.2H_20$ 0.001; $FeCl_3.6H_20$ 0.001. The carbon source glycerol was used at a concentration of 20 mM. The pH was adjusted to 6. 5 with NaOH. All the media were autoclaved at 121°C for 20 min.

Characterisation Studies.

The coal sample received was roll crushed and classified into various size fractions down to 45 microns. All these size fractions were analysed for fixed carbon, volatile matter, moisture and ash (Table 1). The various size fractions were aiso analysed for pyritic sulphur. organic sulphur, sulphatic sulphur and total sulphur contents(Table 2).

Froth Flotation

Around 100 g of representative coal sample was ground to below 100 micron size. The ground material was subjected to flotation in Denver D-12 sub aeration cell at 1500 rpm. Solid concentration was maintained at 10% by using tap water of pH 5.7 and conditioned the slurry with 4g/l kg of light diesel oil for 5 minutes. MIBC concentration was maintained at 30 ppm and the froth was collected at natural pH. Both the concentrate and tailing samples were collected,dried and analysed for total sulphur and iron content which are given in Table 3. The flotation concentrate was sieved into various size fractions. Sulphur and iron contents of each fraction were analysed (Table 4) to assess their distribution. All bioleaching experiments were carried out on the -45 mm fraction.

Bacteria Leaching Tests

For bacterial leaching studies, 90ml of the respective culture medium with 2 g of beneficiated coal (-45 msize) was taken in each flask. Flasks were inoculated with 10 ml of freshly grown Thiobacillus, Pseudomonas aureofaciens and

Rhodococus rhodochorus cultures separately containing 10^6 cells/ml and incubated at 37°C on a shaking water bath. After 12 days, the bioleached coal residues were harvested, washed, dried and analysed for total sulphur by Eschka method [81.

RESULTS AND DISCUSSION

Characterisation studies carried out on the coal sample revealed (Table 1) uniformity in moisture. volatile matter, ash and fixed carbon contents in all the size fractions. The sample was found to contain 1.5% of sulphur as pyritic sulphur out of the total sulphur of6.12% in the sample which means around 24% of the sulphur is associated with pyrite. Table 2 indicates the presence of pyritic and total sulphur in various size fractions. As it can be seen there is hardly any change in sulphur content in all the size fractions.

Flotation test results indicate (Table 3) around 3% by weight could be rejected as flotation tailings containing 11.75% Fe. Although 27% of the iron could be rejected, nearly 98% of the sulphur remained in the flotation concentrate. From this, it can be summarised that the removal of pyrite by flotation was not effective although substantial gangue could be rejected. The iron present in the tailings may be pyrite, goethite as the sulphur present is only 4.96%. As can be seen ftom Table 4, the sulphur to be removed was found to be more or less uniform in all the size fractions of the flotation concentrate.

Table 5 summarizes the results of bacterial leaching in addition to tests using froth flotation followed by bacterial leaching.

Bacterial leaching with all the three types of bacterial strains on the flotation concentrate did not show any encouraging results. Of the three strains, Pseudomonas aureofaciens showed around 15% removal of the total sulphur. But surprisingly, Thiobacillus was found to be totally ineffective in sulphur removal from flotation concentrate. This organism had earlier removed 30% of sulphur from this sample [4]. *Pseudomonas* has shown minor effect as it is a heterotrophic organism and therefore, might have degraded the coated organic flotation reagent. The desired level of sulphur removal could not be achieved which is attributed to the presence of light diesel oil foating on the coal concentrate. Thus, the accessibility of bacteria to attack and remove pyrite particles from coal might have been reduced. Hence, attempts are being made to float the coal after bacterial conditioning of the coal samples so as to compare the results.

CONCLUSIONS

Attempts made to float the coal using light diesel oil with an objective to depress pyrite have met with little success.

Around 15% of total sulphur could be removed from a coal sample of Assam by flotation followed by bacterial leaching using Pseudomonas aureofaciens. However, Thiobacillus was found ineffective in removing the sulphur from the flotation concentrate of the coal. It is presumed that the diesel oil, which was used as collector during flotation of this high sulphur coal must have acted as barrier for this bacterial action. Earlier, Thiobacillusferrooxidans had removed around 30% pyrite from Assam coals. Also a mixed culture of Thiobacillus removed around 38.23% of total sulphur from chemically pretreated Assam coal.

Acknowledgement

The authors wish to express their gratitude to Prof. H. S. Ray, Director, Regional Research Laboratory, Bhubaneswar, for permitting to publish this article. The first author is thankful to CSIR for awarding her fellowship.

REFERENCES

1. K.J. Miller and A.F. Baker, "Flotation of Pyrite from Coal", Bureau of Mines, U. S. Dept. of Interior, Technical Report, 51, (1972).
2. T.D. Wheelock, and T.K. Ho, 'Modification of the Flotability of Coal Pyrites, AIME Annual Meeting", New Orleans, Louisiana, pp. 18-22 (1979).
3. G.F. Andrews and J. Maczuga, in "Biotech. and Bioengineering Symposium No. 12", Wiley, New York, pp.337-348 (1982).
4. C. Acharya, R.N. Kar, S.K. Mishra, I. Twardoska and L.B. Sukla, 'Microbial Depyritization of Assam Coal", Indian J. of "crobicl., 37, pp. 17-20 (1997).
5. B. Osipowicz, L. Jaflonski, A. Siewinski, S. Jasienko, and A. Rymkiewicz, 'Biodegradation of hard coal and its organic extract by selected microorganisms", Fuel, 73, pp. 1858-1862 (1994).
6. T.O. Bozdemir, T. Dunsoy, E. Erinum, and Y. Yunum, "Biodesulphurization of Turkish Lignites", Fuel, 75, pp. 1959-1600 (1996).
7. Z.M. Dogan, G. Ozbayoglu, C. Kicyilmaz, M. Sarikaya, and G. Ozcengiz, 'Macterial leaching versus bacterial conditioning and flotation in desulphurization o 1 three different coals", Proceedings of the Sixth International Symposium on Biohydrometallurgy, Vancouver, B.C., Canada, 4, pp. 165-169 (1985).
8. Indian Standard Methods of Test for Coal and Coke, Part III, determination of sulphur (First Edition), IS : 1350 (Part III), Bureau of Indian Standards (1969).
9. S.S., Tripathy, R.N., Kar, S.K., Mishra I. Twardowska, and L.B., Sukla, Fuel, 1998,77(8),859-864.

Table-I

Proximate analysis of various size fractions of coal

Size, µm	Wt.%	Constituents,%				Distribution %			
		Moisture	Volatile matter	Ash	Fixed Carbon	Moisture	Volatile Matter	Ash	Fixed Carbon
-210+150	59.8	2.10	39.3	3.60	55.0	57.0	60.3	55.4	59.9
-150+75	14.4	2.10	39.0	3.20	55.7	13.7	14.4	11.8	14.6
-75+45	10.4	2.20	39.0	3.60	55.2	10.4	10.4	9.64	10.4
-45	15.4	2.70	37.8	5.00	53.7	18.9	14.9	19.8	15.1
Calc (Head)	100	2.20	38.94	3.88	54.9				

Table-II

Analysis of sulphur in various size fractions of coal

Size, µm	Wt.%	Sulphur,%			Distribution, %		
		Pyritic	Organic+Sulphatic	Total	Pyritic Sulphur	Organic+Sulphatic	Total Sulphur
-210+150	59.8	1.46	3.94	5.40	58.1	60.9	60.1
-150+75	15.4	1.96	2.71	4.67	20.1	10.8	13.4
-75+45	10.4	1.36	3.83	5.19	9.0	10.3	10.0
-45	14.4	1.29	4.83	6.12	12.4	18.0	16.4
Calc (Head)	100	1.50	3.867	5.369	100		

Table-III

Analyses of flotation products

Flotation Products	Wt.%	Assay,%		Distribution,%	
		S	Fe	S	Fe
Concentrate	97.1	5.90	0.95	97.9	73.0
Tailings	2.9	4.36	11.75	2.1	27.0
Calc (Head)	100	5.855	1.26	100	100

Table-IV

Assay of Fe, S in various size fractions of flotation concentrate

Size,μm	Wt%	Assay %		Distribution %	
		S	Fe	S	Fe
+100	14.83	5.58	2.00	14.73	34.93
-100+75	53.15	5.53	0.22	52.34	57.83
-75+45	21.17	6.27	0.22	23.64	4.8
-45	10.81	4.82	0.25	9.28	3.2
Head (Calc)	100	5.615	0.83	100	100

Table-V

Percentage removal of sulphur from Assam coal (-45μm) under various test conditions

Sl.No.	Test Conditions	pH	Total sulphur	% Total sulphur removal
1.	Bacterial leaching	1.7	3.92	24.29[4]
2.	Chemical pretreatment and bacterial leaching (112.5 mm size fraction)	2.5	5.55	38.23(9]
3.	Flotation and leaching with *Thiobacillus*	2.5	5.58	Nil
4.	Flotation and leaching with *Pseudomonas aureofaciens*	7.0	5.58	15
5.	Flotation and leaching with *Rhodococcus rhodochorus*	6.5	5.58	3.34

38TH ANNUAL MEETING OF THE ASSOCIATION OF MICROBIOLOGISTS OF INDIA CONFERENCE ON MICROBES IN SUSTAINABLE DEVELOPMENT

Platinum Jubilee
University
of Delhi

Silver Jubilee
South Campus
University of Delhi

ABSTRACTS

Venue :
JAMIA MILLIA ISLAMIA, NEW DELHI

DEC. 12 - 14, 1997

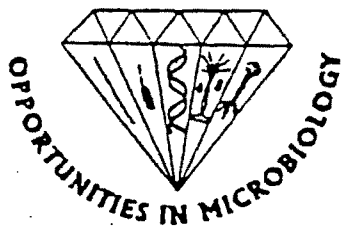
Organised by :
DELHI UNIT II OF AMI
Jointly with University of Delhi, South Campus, Jamia Millia Islamia
NII, JNU, IARI and IIT Delhi

EM-6 - BACTERIAL DESULPHURISATION OF COAL SAMPLES FROM ASSAM WITH AND WITHOUT FLOTATION PRETREATMENT

C.ACHARYA[1], R.N.KAR[1], I. TWARDOSKA[2], L.B.SUKLA[1]

[1]Regional Research Laboratory, Bhubaneshwar-751 013
[2]Institute of Environmental Engineering, Polish Academy of Sciences, Poland

Desulphurisation of coal by bacterial leaching is very effective. Several different organisms have been suggested for coal desulphurisation. Also, among the physical and chemical coal cleaning techniques, froth flotation is very effective in removing pyrite from high sulfur coal. In the present investigation, *Pseudomonas aureofaciens*, *Rhodococcus rhodochorus* and mixed culture of *Thiobacillus ferrooxidans* and *T.thiooxidans* were compared with mesophilic bacterium *T.ferroaxidans* concerning their capability of removing sulfur from coal samples of Assam with and without flotation. Without flotation, *T.ferroxidans* could remove around 30% pyrite from the coal samples. Floated residue when subjected to bacterial leaching yielded a maximum removal of total sulfur of 15% with *P.aureofaciens*.



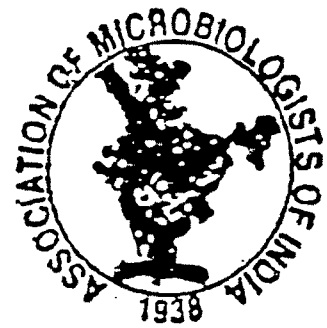
DIAMOND JUBILEE SYMPOSIA

AND

39TH ANNUAL CONFERENCE

ASSOCIATION OF MICROBIOLOGISTS OF INDIA
MANGALORE, DECEMBER 5-7, 1998

ABSTRACTS & PROCEEDINGS



MANGALORE UNIT OF AMI
DEPARTMENT OF MICROBIOLOGY
UNIVERSITY OF AGRICULTURAL SCIENCES
COLLEGE OF FISHERIES, MANGALORE - 575 002.

IMB-58. BIOLEACHING OF LOW GRADE MANGANESE ORE USING NATIVE MICROORGANISMS

C. Acharya, R.N. Kar and L.B. Sukla
Regional Research Laboratory (CSIR), Bhubaneswar, Orissa.

Native microorganisms present in mineral deposits and mines are known to be tolerant to metals present in their habitat. Therefore, microbial strains were isolated from the top soil sample of Joda East manganese ore mines of Orissa using enrichment medium for fungi and bacteria separately. Strains were purified by repeated streaking and single colony isolation methods. Growth patterns and colony morphology were recorded. In total, three bacterial and five fungal isolates were purified. Manganese leaching ability of individual strains were examined using a low grade manganese ore containing 27.2% Mn in respective liquid medium. Out of eight microbial isolates, maximum manganese solubilization to the extent of 18% was achieved with a fungal isolate. Hence, with this strain the effect of different parameters like pulp density, particle size, concentration of sucrose and size of inoculum were studied. An extraction of 15.20% Mn could be achieved with 10% (w/v) sucrose, 2%(w/v) pulp density and 10(w/v) inoculum size.