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ORIGINAL ARTICLE

Bioleaching of low-grade uranium ore using *Acidithiobacillus ferrooxidans*

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Abstract Bioleaching of uranium was carried out with Turamdih ore sample procured from Uranium Corporation of India Limited, Jaduguda. The bacterial strain that was used in the leaching experiments was isolated from the Jaduguda mine water sample. Efficiency of bioleaching was studied by varying parameters like pulp density and initial ferrous concentration as source of energy. It is observed that the efficiency of bioleaching was 49% at 10% pulp density (w/v) and initial pH 2.0. Addition of external has no effect on efficiency of bioleaching showing domination of direct leaching mechanism over indirect.

Keywords Uranium · Bioleaching · *Acidithiobacillus ferrooxidans*

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Introduction

The increasing use of uranium in nuclear power industry as well as in the generation of electricity and an alternative source of energy in shipping industries has resulted in progressive exhaustion of high-grade uranium reserves. Therefore in order to accommodate the demand, modern techniques are being developed for recovery of uranium in a commercial scale. Uranium is an important natural resource used for the generation of nuclear energy, as the raw material for the production of uranium oxide U_3O_8 [1]. Uranium is extracted conventionally using a process that employs strong acids as reagents, which often creates environmental problems, requires large amounts of energy, and involves a complex operational plant. It is not economical to extract uranium from low-grade ores by chemical leaching because the content of uranium ore is very low by weight [2]. Hence it is necessary to build up an alternative process to facilitate the efficient and economic recovery of the uranium. Bioleaching of low-grade ores is becoming a popular alternative since it is an economically viable phenomenon moreover the microorganisms used in these processes are able to grow in highly acidic environments with high heavy metal content (U and Th). Therefore this technique is proving to be a profitable alternative to the conventional processes [3].

In the present paper, an effort has been made to study the feasibility of *Acidithiobacillus ferrooxidans* in leaching U from the low-grade uranium ore of Turamdih mines. Oxidation of ferrous ion into ferric is one of the characteristic property of *A. ferrooxidans*. The ferric ion acts as an electron acceptor and converts U^{+4} to U^{+6} state which is soluble in water, hence the metal is leached out to the liquor solution.

$$UO_2 + Fe_2(SO_4)_3 \longrightarrow UO_2SO_4 + 2FeSO_4 \quad (1)$$

$$2FeSO_4 + 1/2O_2 + H_2SO_4 \xrightarrow{\text{Bacteria}} Fe_2(SO_4)_3 + H_2O \quad (2)$$

Since the bioleaching phenomenon involves living organisms, hence the yield of metal leaching is influenced by various environmental, biological and physicochemical factors [4, 5]. Therefore efficiency of bioleaching with various parameters such as pulp density, initial pH, initial ferrous concentration, availability of oxygen has been studied.

Materials and methods

The microorganism used in the bioleaching study was isolated from the Turamdih mine water sample at the Institute of Minerals and Material Technology (formerly Regional Research Laboratory), Bhubaneswar. Prior to bioleaching experiments, the strain was revitalized in freshly prepared 9K medium [6].

The obtained ore samples were subjected to acid neutralization studies followed by which the bioleaching process was commenced [7, 8].

Concentrations of ferrous and total iron in the medium were analyzed by the titration method using 0.1N potassium dichromate as titrant and barium diphenylamine-4-sulfonate (BDAS) as redox indicator. Concentration of ferric iron was calculated by subtracting concentration of ferrous from total iron [9]. The uranium analysis was done by flourimetry method at Uranium Corporation of India Limited (UCIL), Jaduguda.

Quantitative composition of raw uranium ore sample was carried out in the laboratory using a wavelength-dispersive X-ray fluorescence spectrometer.

Experimental

All the experiments were carried out with total content of 100 ml using 250 ml Erlenmeyer flasks at 30ºC and 150 rpm in a Kuhner incubated shaker. Samples were collected regularly to check, pH, Eh and for analysis of Fe(II) and Fe(III) concentration. Also samples were prepared regularly for uranium analysis in 10% HCl.

Unless otherwise specified the experimental conditions were pH 2.0, temperature 30ºC, 10 ml inoculum and initial Fe(II) concentration of 9 g/l.

Results and discussion

Prior to leaching experiments, the isolated culture was cultivated in 9K media. Repeated subculturing was carried out continually until a constant iron oxidation rate was achieved.

Composition of the designated low-grade uranium ore is shown in Table 1. From the table, it was confirmed that it was quartz-chlorite-sericite ore with significant amount of hematite and apatite having 0.04% of U_3O_8, which promotes the mass transfer by shrinking model and ultimately favors bioleaching process. Percentage of acid consuming minerals such as Na, Mg, K and Ca was more than 8%. This might cause the elevation of pH during bioleaching, which could inhibit the overall process because of several reasons. Firstly the bacterial growth is very sensitive to pH of the nutrient medium. Secondly availability of proton decreases with increasing pH which causes the retardation of oxidation reaction. More over formation of product layer on the surface of ore particles at higher pH makes contact barrier between ore particles and metabolites. Hence dissolution of the acid consuming minerals was a pre-requisite to the bioleaching experiments. In the other hand the leaching studies were proposed to be carried out with the acidophilic microorganisms hence it was mandatory to maintain the pH of the leaching environment between pH 1.5–2.5 debarring which, the bacteria would loose its activity. Therefore it was thought worthwhile to undertake pre-acid neutralization before leaching. For this purpose the ore was treated with dilute sulfuric acid at pH 2.0. The acid neutralization

Table 1 Quantitative composition of raw low-grade uranium ore sample

Contents	Concentration in %
U_3O_8	0.037
Na_2O	0.4
MgO	3.812
Al_2O_3	8.436
SiO_2	66.83
P_2O_5	2.063
SO_3	0.185
K_2O	2.236
CaO	2.205
TiO_2	0.405
Cr_2O_3	0.041
MnO	0.039
Fe_2O_3	12.22
NiO	0.088
CuO	0.026
Rb_2O	0.014
MoO_3	0.024
F	0.801
Cl	0.116

continued till a steady state of pH was attained. In the total neutralization process acid consumption was calculated to be 90 g/kg as against 128 g/kg of ore as per theoretical calculation based on the ore analysis. The difference in acid consumption between the actual and theoretical one may be due to non-dissolution of acid consuming gangue mineral. In the entire acid neutralization step the uranium dissolution was around 3%. Finally neutralized ore was kept in oven at 50ºC up to dryness. The same material was used in the bioleaching process.

The isolated bacterial culture was adapted to the reaction medium by several sets of subculturing. During the initiation of adaptation study the bacterial lag phase was observed to continue for several days. Followed by numerous sets of subculturing of the whole biomass, the bacterial log phase was initiated immediately after inoculation and the iron oxidation rate of the adapted bacterial culture was observed to be 658 mg/l/h. Assuming the iron oxidation to be first order, the plot of $-\ln[Fe(II)_t/Fe(II)_o]$ versus t would give a straight line. The specific reaction rate was calculated to be 0.168/hour. Accurate bacterial count could not be reported as *A. ferrooxidans* strains have an inherent property to adhere to the walls of the container as well as to the ore particles [10], hence the bacterial growth rate was indirectly monitored by measuring the ferrous oxidation rate.

Since uranium dissolution from the ore requires an oxidant therefore the leaching studies were carried out in presence of ferrous sulfate at different pulp density. The initial iron concentration was 9 g/l. The pulp density was varied from 5% to 20%. Figures 1 and 2 show the Fe(II) and Fe(III) concentration for different days for the leaching studies containing bacteria and control, respectively. The iron oxidation rate in presence of bacteria was very high and within 7 days all the Fe(II) was oxidized to Fe(III) where as in control the iron oxidation rate was very slow. Table 2 shows the iron oxidation rate for leaching studies carried out in presence and absence of bacteria. Assuming that no iron is being leached out from the ore in both the cases, hence, once the iron is oxidized it started precipitating. Table 3 shows rate for leaching studies carried out in presence and absence of bacteria, respectively.

Figure 3 shows the reaction time of leaching carried out in presence of bacteria with ferrous sulfate; control with ferrous sulfate and bacteria without ferrous sulfate at 10% pulp density. It can be observed that bioleaching of uranium was efficient than chemical control at same conditions. In presence of bacteria with ferrous sulfate, the leaching path was observed to be in 3 stages within 32 days. In the first stage up to 7 days, it was very fast. From day 7 to day 20, the rate was little bit lower and it became parallel to the control path after 20 days. This means that after 20 days the leaching process was retarded due to the formation of product layer on the ore surface which created a contact barrier between ore particle and bacterial cell wall for further metabolism. From Figure 2 it can also be confirmed that the concentration of ferric ion in leaching medium was 1.5 g/l on day 20 which shows that significant part of ferric ion may be hydrolyzed to form precipitate. Previously it was observed that iron precipitates when Fe(II) was oxidized to Fe(III). The precipitation of iron would definitely form a product layer over the ore which may retard the uranium mineral dissolution. Bioleaching in presence of bacteria without ferrous sulfate shows little difference from that presence of ferrous sulfate showing the efficiency of leaching was very

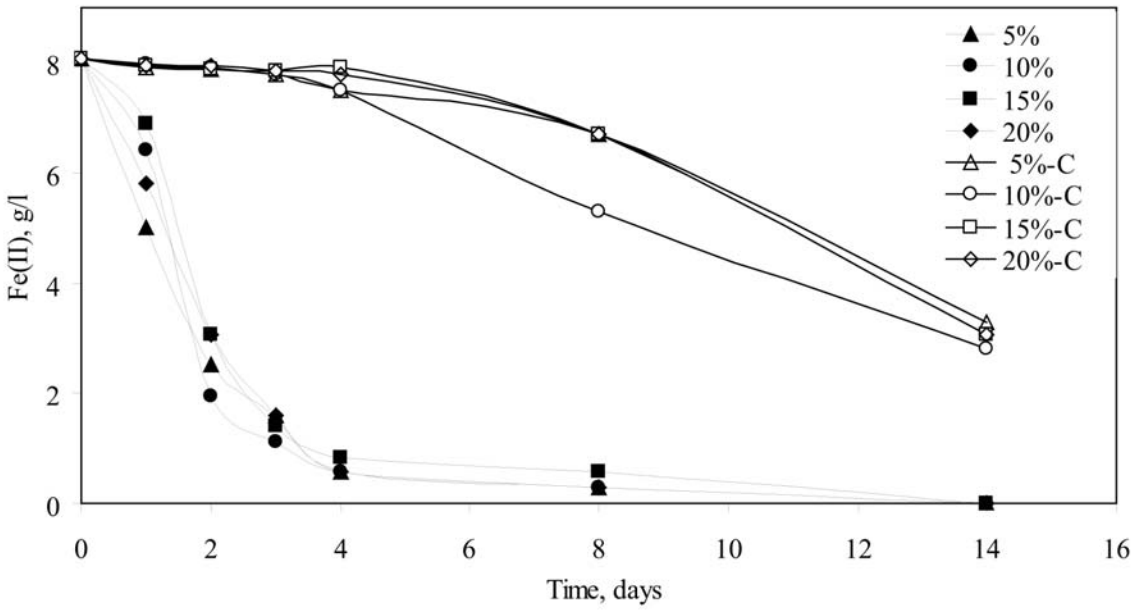

Fig. 1 Variation of ferrous concentration during U bioleaching at various pulp density with respective controls.

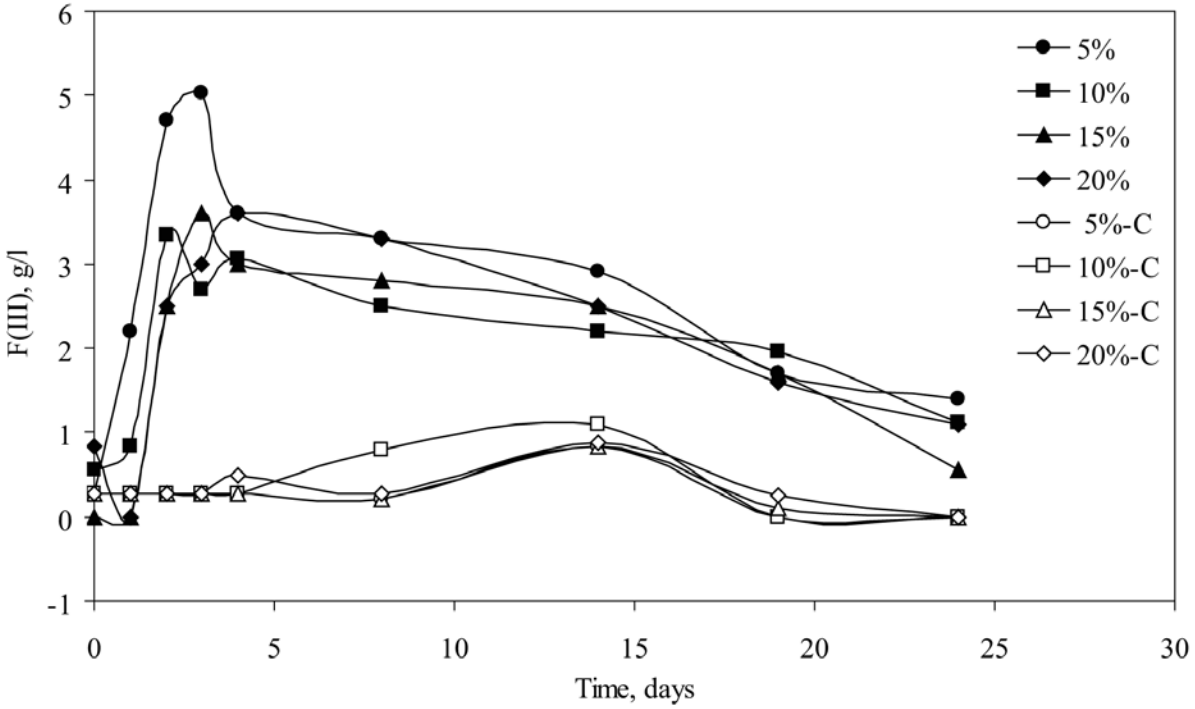

Fig. 2 Determination of iron precipitation rate at various pulp density with respective controls.

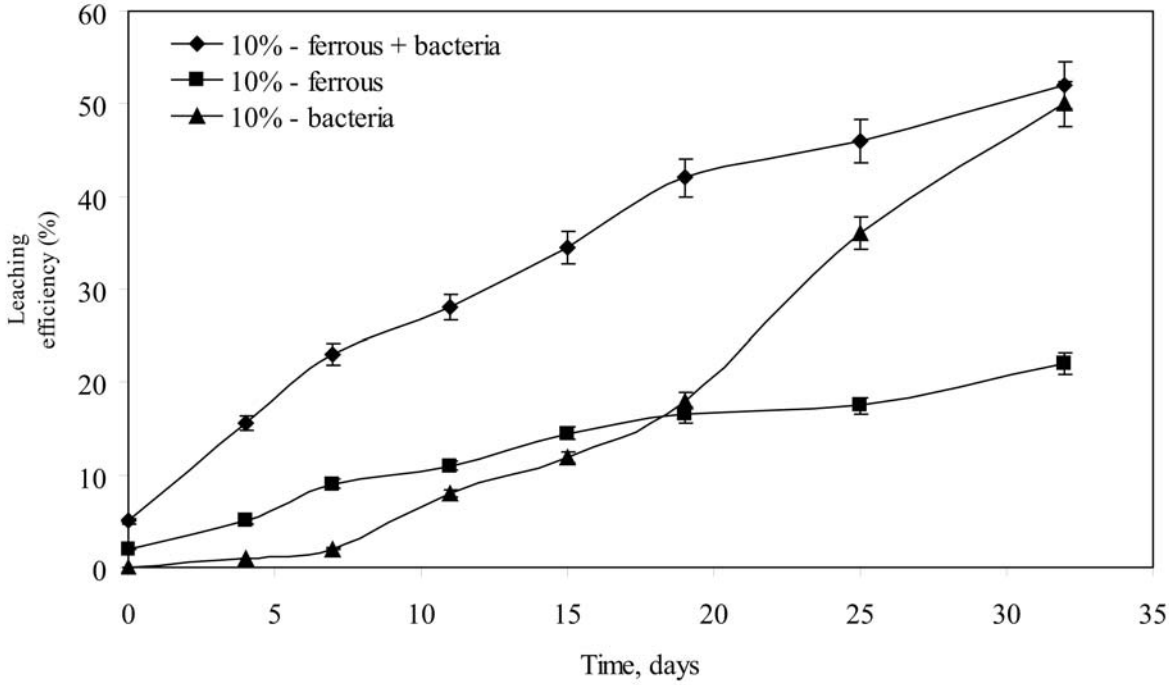

Fig. 3 Effect of reaction time at different conditions. Conditions: 10% pulp density, initial pH 2.0, 30°C and 150 rpm.

Table 2 Iron oxidation and precipitation rate during bioleaching of uranium at various pulp densities

Parameter Pulp density	Iron oxidation rate (g/l/day)		Iron precipitation rate (g/l/day)	
	With bacteria	Control	With bacteria	Control
5%	1.99 ± 0.1	0.068	0.156 ± 0.01	0.007
10%	2.18 ± 0.2	0.063	0.097 ± 0.009	0.013
15%	2.06 ± 0.2	0.02	0.129 ± 0.01	0.014
20%	2.08 ± 0.2	0.13	0.145 ± 0.01	0.01

Table 3 Uranium dissolution varying pulp densities with different conditions

Pulp density (w/v)	Uranium dissolution rate		
	Bacteria + $FeSO_4$ mg/g ore/day	Control + $FeSO_4$ mg/g ore/day	Without $FeSO_4$ mg/g ore/day
5%	0.0044	0.0025	0.0037
10%	0.0052	0.0028	0.0051
15%	0.0055	0.0022	0.002
20%	0.0046	0.0018	0.0014

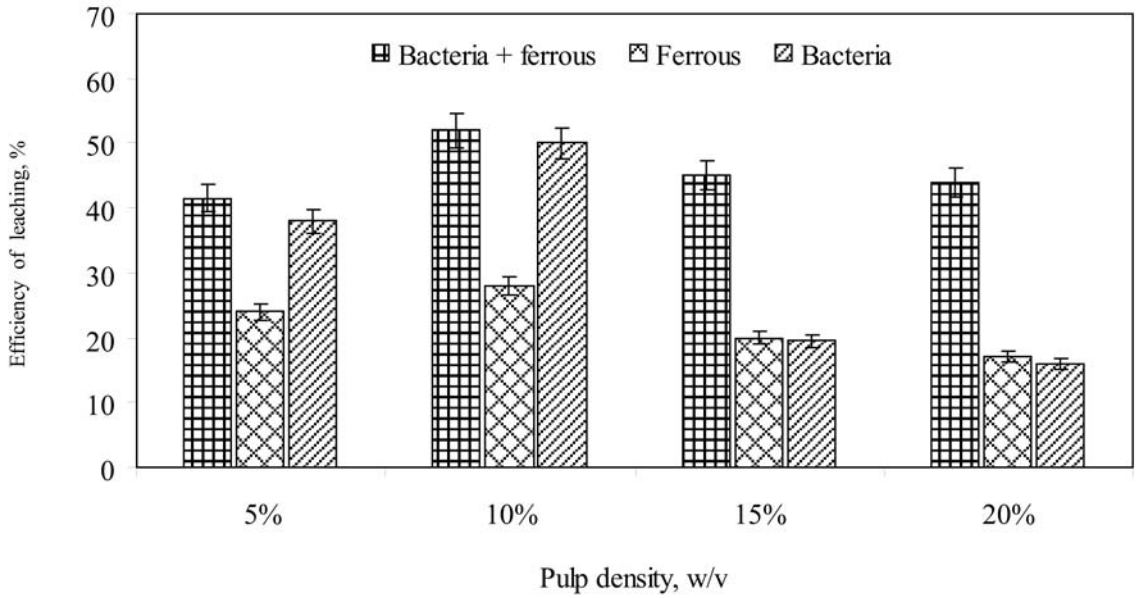

Fig. 4 Efficiency of bioleaching at different pulp density.

fast after 20 days of starting the experiment. This may be due to the substantial dissolution of hematite present in the ore in the initial stage of experiment. Hence leaching was commenced after 7 days of starting experiment. Nutrient addition to the solution in which the bacterium and Fe(II) were present resulted in no significant increase in the extent of U leaching relative to Fe(II)-bearing, oligotrophic condition. The results might be due to natural supply of inorganic nutrients to the cells from the low-grade uranium ore [11].

The efficiency of uranium bioleaching increases with the increase in pulp density up to 10% and further increase in pulp density shows a reverse trend. A similar trend was also observed in case of control. Therefore it may be concluded that the decrease in efficiency of leaching may be due to lack of oxygen or improper mixing between the lixiviant and ore particle or both. The leaching rate increased uniformly through out the experiment as the easily oxidizing uranium minerals were solubilized during preneutralization step. The uranium dissolution rate for different pulp density is shown in Table 3. Therefore it is thought worthwhile to carryout leaching in the absence of external addition of iron. Results are shown in Figure 4. By comparing the leaching rate in presence and absence of external addition of iron made hardly any difference. In this case too the percentage of leaching increases with increase in pulp density up to 10% and beyond that it shows a reverse trend.

Since the percentage of uranium recovery was observed to be highest at 10% pulp density, hence a statistical correlation was carried out with the same. The coefficient of variance (CV) for 10% pulp density at different reaction conditions, varied from 0 to 0.1%.

Conclusion

Bacterial leaching studies were carried out after neutralization of the ore. During neutralization around 3% of U was leached out. The percentage of U leaching was observed to be same in presence and absence of external addition of iron. The percentage of U leaching increases up to 10% pulp density and beyond that it showed a reverse trend. Looking at the leaching rate it can be concluded that the ore is amenable to bacterial leaching.

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