16th International Conference on Non-ferrous metals 2012
New Delhi
Eds: Dr. Abhilash, Dr. Prabhakar Landge & Prof. T R Mankhand

BIOREACTOR LEACHING OF URANIUM FROM A LOW GRADE INDIAN ORE

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Abstract:

Bio-leaching studies were carried out in a 2L bioreactor- BIOSTAT-B® equipped with a PLC based controller at 20-40% (w/v) pulp density using enriched culture of A.ferrooxidans for Turamdih uranium ore (Jharkhand, India). With the enriched culture of A.ferrooxidans adapted on Fe(II) at pH 2.0, 35°C and 20% (w/v) pulp density, a 98.3% uranium recovery was recorded in 14 days. The leaching of uranium in the bioreactor improved the dissolution rate by reducing the time from 40 days in shake flask as per our earlier studies to 14 days. While investigating the importance of biogenic Fe (III) in the bio-leaching process a maximum recovery of 84.7% U_3O_8 was observed at pH 2.0 and 20% (w/v) pulp density in 10h as compared to the uranium leaching of 38.3% in the control experiments. On raising the pulp density to 30%, uranium bio-recovery increased to 87.6% in 10h at pH 2.0 with <76μm size material. This showed a distinct advantage because of better mixing of slurry in the bioreactor with auto-controlled conditions that improved the kinetics.

Keywords: *low-grade ore, uranium, A.ferrooxidans, bioreactor, biogenic Fe(III)*

1. INTRODUCTION

Uranium is conventionally recovered from its ores by chemical method following acid or alkali leaching using an oxidant, and is enriched by ion-exchange/solvent extraction process to precipitate magnesium diuranate [Abhilash and Pandey, 2012]. The continued depletion of high grade ores and growing awareness of environmental degradation associated with the traditional methods have provided impetus to explore simple, efficient and less polluting biological methods in uranium mining, processing and waste-water treatments [Abhilash et al., 2011]. Hydrometallurgical methods have some disadvantages such as lower recovery, involvement of high process and energy cost and increase in pollution load of water resources [Torma and Banhegyi, 1984]. Uranium could also be recovered by microorganisms that catalyze the oxidation and reduction of uranium and associated metals also and hence influence their mobility in the environment [Abhilash and Pandey, 2012]. The uraninite in Jaduguda, Bhatin and Narwapahar ores is entirely UO_2 (IV) and UO_3 (VI) types and hence UO_2(IV) remains undissolved or dissolve

slowly in the absence of iron in traditional method [Dwivedy and Mathur, 1995]. The use of solid-liquid leaching technique as unit operation (H_2SO_4/MnO_2, $NaClO_3$, $Fe_2(SO_4)_3$ or pyrolusite leaching) is the most important process by which uranium ores are being processed in India [Mathur et al., 1992; Mathur et al., 2000]. It is reported that at 1 kg/T ferric sulphate consumption with 1kg/T acid, the same amount of uranium can be leached with 20 kg/T of acid and 4 kg/T pyrolusite. The sulphate leach liquor (pH 1.0- 2.0) typically carries 0.5-0.6 g/L uranium and other impurities like Fe, Al, V, Cu, Mn etc. in varying concentrations depending on the nature of the mineral and leaching conditions employed [Abhilash and Pandey, 2012].

For a country with limited energy resources and for long-term energy security bioleaching exploiting microorganisms is an alternative, highly selective, eco-friendly and economically attractive option [Abhilash et al., 2011]. The procedures are not complicated and are easy to control and extensive technical knowledge is not required. Moreover, the microorganisms used in this processes are able to grow in acidic environment with high metal content like U, Th, Cu, Ni [Torma and Banhegyi, 1984].

The objective of the work presented in the thesis is to study the bioleaching of uranium from Turamdih ore and optimisation of parameters in lab scale bioreactor.

2. MATERIALS AND METHODS

Uranium ore collected in the form of lumps from Turamdih mine was crushed, ground and sieved to get different size fractions. A representative sample was prepared by coning and quartering for chemical analysis. The uranium content (U_3O_8) was calculated to be 0.024% with 10.64% Fe and 47.4% SiO_2. The phase identification by XRD [SIEMENS™ Model: SIEFERT 300] shows that quartz, alumina and magnetite are the major phases while kyanite (aluminium silicate), apatite, ferrosilite (ferro-silicate), pyrite and hematite being the minor phases. Uranium is present as uraninite in the ore [Rao and Rao, 1983; Sarangi and Krishnamurthy, 2005].

Mine water sample collected from Turamdih uranium mines was the source for isolation of *A. ferrooxidans* in 9K media at pH 2.0. The oxidation of Fe(II) to Fe(III) by *A. ferrooxidans* was considered as an indication of its growth, which in turn was also monitored using Leica™ Biological Microscope. The isolated enriched culture of *A.ferrooxidans* was adapted on 5%(w/v) ore of <100µm size for three times at pH 2.0 and 35°C; the adapted culture was used for the bioleaching [Abhilash et al., 2009]. Uranium was analysed by Flourimetry [Model-FL-6224™] whereas other metals were analysed by Atomic Absorption Spectrometer [Model-GBC 908BT™].

Bio-leaching studies were carried out in a 2L bioreactor- BIOSTAT-B® (Make-SARTORIUS-**Fig.1**) at 20-40% (w/v) pulp density using 10%(v/v) enriched culture of *A.ferrooxidans*. In each case, a known amount of sample was taken and desired pH, stirring speed (150rpm) and temperature were maintained by PLC based MFCDA™ software controlled operations in the reactor. Experiments were carried out by using bacterial culture and also by biogenically prepared Fe (III) solution. The fresh culture of *A.ferrooxidans* was adapted on 10g/L Fe(II) (in a sequence of 5g/L and 10g/L

Fe(II)) using 10% (v/v) *A.ferrooxidans* with bacterial population of $6x10^6$ cells/mL in the total volume of 1L in the 2L bioreactor under electronically controlled conditions of pH 2.0, 150 rpm and 35°C. Biogenic ferric sulphate was generated from a synthetic ferrous sulphate solution [10 g/L Fe(II)] at pH 2.0 and 35°C. The final solution containing Fe(III) enriched with *A.*ferrooxidans ($1.7x10^8$ cells/mL) and redox potential of 510 mV was obtained under this condition in 96h. The 10% inoculum (biogenically prepared solution) was used to make the slurry with the ore at the desired pulp density for optimization of parameters to understand the role of Fe(III) ions and bacteria. The bioreactor was equipped with a sampling port to timely withdraw slurry for estimating metal and bacterial concentrations. As mentioned earlier, ferrous ion concentration was analyzed by titration against N/10 potassium dichromate solution. The pH of the leach slurry in reactor was maintained automatically with 5 M sulfuric acid solution. Redox potential was measured against SCE. On completion of the experiment, the leach liquor was filtered with Whatman No.42 paper, and the residue was dried in oven and analyzed for residual uranium concentration.

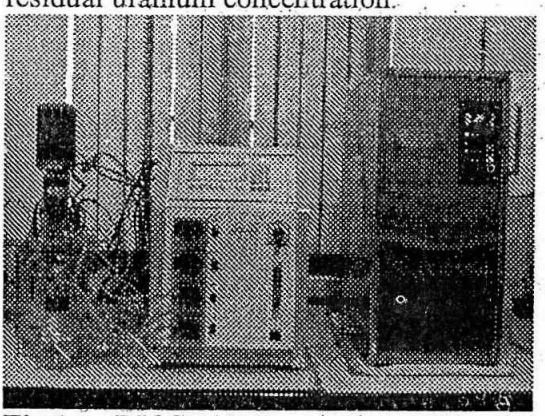

Fig.1: BIOSTAT-B (2L) used for laboratory scale bioreactor leaching of uranium

3. RESULTS AND DISCUSSION

3.1. Uranium bioleaching with enriched (adapted) culture of A.ferrooxidans:

The bioleaching of uranium from Turamdih ore was carried out in the 2L bioreactor using enriched (adapted) culture of *A.ferrooxidans*. The conditions maintained during the bioleaching at pH 2.0 were: 20% (w/v) pulp density, 35°C, 150rpm using ore particles of <76μm (mixed) size with 10% (v/v) inoculum of enriched bacteria unless stated otherwise. The experiments were conducted for 14days while recording the redox potential and biodissolution of uranium is reflected in Fig.2.

It is interesting to see that almost 30% uranium was recovered within 1 day which increased to 74% in 12 days at the redox potential of 700mV. Further leaching beyond 12 days resulted in drastic increase in uranium bio-recovery (98.3%) in 14 days; the redox potential was recorded to be 754mV at this stage. This trend in dissolution behaviour may be accounted for prevalence of strong oxidizing conditions established with high E value (700mV) in 12 days time. As compared to 96% uranium leaching in the shake flask experiments at pH 2.0, 35°C and 20% (w/v) pulp density in 40 days time [Abhilash et al., 2009], the leaching in bioreactor was 98.3% within 14 days. This showed a distinct advantage because of better mixing of slurry in the bioreactor with auto-controlled conditions that improved the kinetics [Ahonen and Tuovinen, 1995].

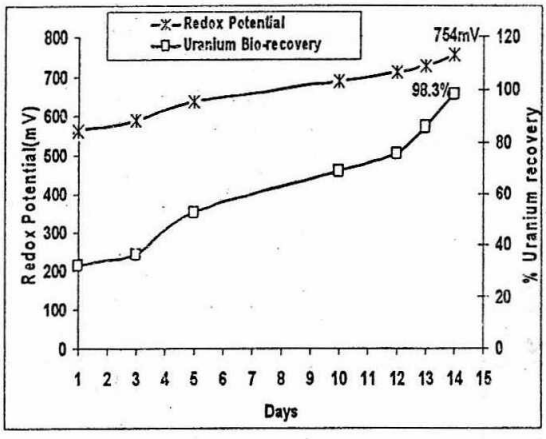

Fig.2: Uranium biorecovery with variation in redox potential using enriched *A.ferrooxidans* [pulp density:20% (w/v), T:35°C, particle size: <76µm, pH: 2.0]

3.2. *Uranium bioleaching with biogenic iron (III) solution:*

Although, the leaching of uranium in the bioreactor has improved the dissolution rate by reducing the time from 40 days to 14 days, the importance of using biogenic Fe(III) in the bio-oxidation process can be emphasized as it plays a major role [Abhilash and Pandey, 2011]. Thus, bioleaching in presence of Fe(III) can be exploited to achieve higher rate of leaching . Therefore, further experiments were carried out with enriched culture of *A.ferrooxidans* and biogenic Fe(III), and parameters were optimized.

3.2.1. Effect of pH: The effect of varying pH from 2.0 to 2.5 at 20% (w/v) pulp density, 35 °C temperature and 150 rpm with <76µm size particles on bioleaching of uranium was examined in 1L volume of 2L BIOSTAT; data are presented in Fig. 3. Experiments could not be carried out at pH below 2.0 due to the limitation of the available reactor which has a configuration of pH in the range 2.0-14.0. An appreciable increase in bio-recovery of uranium (84.7%) at pH 2.0 with an increase in redox potential from 536–674 mV in 10h was observed as compared to the low uranium leaching (38.3%) in the control experiments (Fig.3) with low E value (448mV) during this period. The bio-recovery was 74% and 67% at pH 2.2 and pH 2.5 respectively with corresponding rise in redox potential from 532–646 mV and 533–603 mV (Fig.4a).

The lower metal bio-recovery at pH>2.0 may be the result of lower oxidation potential of leaching system, decreased bacterial cell count (Fig.4b), and precipitation of higher amount of iron(III) as hydronium jarosite [Abhilash and Pandey, 2011]. Higher uranium biorecovery (84.7%) at pH 2.0 may be attributed to the enhanced level of oxidation of U(IV) by biogenic Fe(III) initially available and produced due to bacterial oxidation. Uranium bioleaching at this pH may also be correlated with very high redox potential value (674 mV) acquired during the process (Fig.4a).

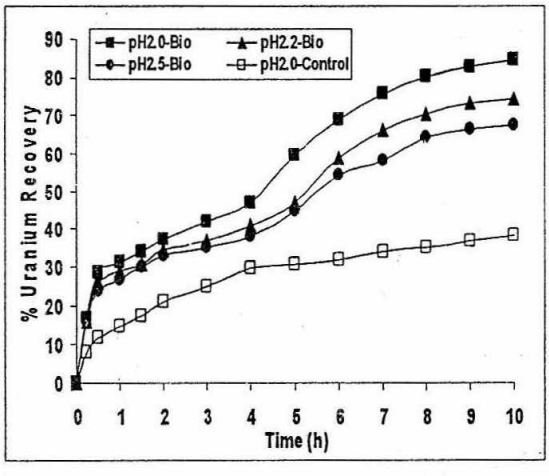

Fig.3: Uranium recovery at various pH in bioreactor at 20% (w/v) pulp density, 35°C with <76µm particles with biogenic Fe(III) [Fe(III):10g/L; rpm:150]

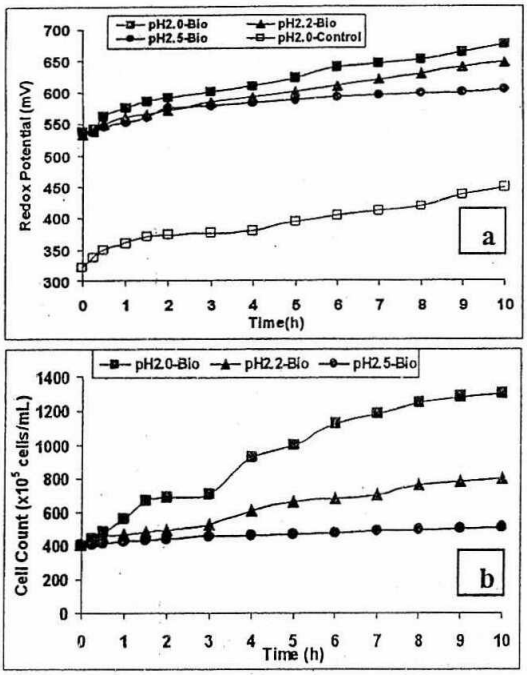

Fig.4: Change in **(a)** redox potential and **(b)** cell count at various pH in bioreactor at 20% (w/v) pulp density, 35°C with <76µm particles with biogenic Fe(III) solution {Fe(III) in feed:1g/L} against control leaching

The bacterial action after 1 h of the experimentation might have facilitated conversion of Fe(II) to Fe(III) (Fig.5) resulting in high rate of oxidation of U(IV) to U(VI) and consequently higher uranium bio-recovery was maintained [Sand et al., 2001]. Higher (1.2 g/L) concentration of Fe(III) at pH 2.0 appears to be associated with high bacterial activity which is evident from increased cell population($1.3x10^8$ cells/mL in 10d), besides some iron dissolution from the ore. On the other hand, lower iron oxidation rate in control experiments (Fig.5) would be responsible for lower metal recovery. The presence of low Fe(II) level and high amount of Fe(III) produced biogenically, yielding high uranium recovery suggests that indirect leaching mechanism is responsible for uranium bio-dissolution [Abhilash et al., 2009; Abhilash and Pandey, 2011].

3.2.2. Effect of pulp density: Pulp density for the bioleaching of uranium in bioreactor was varied in the range 20–40% (w/v) using <76µm size particles by 10% (v/v) inoculum containing ~0.8g/L Fe(III), while shaking at 150 rpm at pH 2.0 and 35°C temperature. At 20% (w/v) pulp density (Fig.6), uranium recovery of 84.7% was obtained in 10h. On further increasing the pulp density to 30% (w/v) and 40% (w/v), the uranium bioleaching was found to be 87.6% and 80% respectively. The rise in E was observed to be 674, 690 and 642mV in bioleaching at 20% (w/v), 30% (w/v) and 40% (w/v) pulp density, respectively in 10h. It may be mentioned that at 30% (w/v) pulp density, the uranium leaching was maximum (87.6%), which decreased to 80% at still higher pulp density of 40% (w/v) (Fig.6) because of lower ratio of inoculum to substrate [Abhilash et al., 2009].

3.2.3. Effect of particle size: Effect of particle size on bio-dissolution of uranium is presented in Fig.7. The bio-recovery was found to be 87.6% in 10h at pH 2.0 and 30% (w/v) pulp density with the ore particles of <76µm size as compared to 86% and 76% uranium biodissolution for 53-45µm and <45µm size materials. This may be attributed to better permeation of the microbe and Fe(III) rich lixiviant in the <76µm size particles to oxidise uranium present in the ore. It may thus be reasonable to conclude that better permeation of lixiviant takes place with the mixed size fractions resulting in the higher metal recovery as compared to the particles of very fine size. The lower uranium recovery with the finest size ore (<45µm) may be caused by lesser

permeation of the lixiviant as such particles are likely to be less dispersed in the system lowering the microbial action on them [Abhilash and Pandey, 2011].

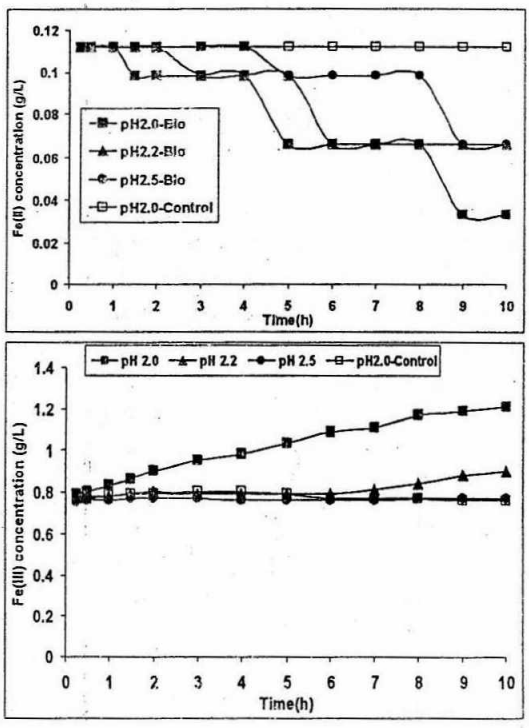

Fig.5: Change in Fe(II) and Fe(III) concentration at various pH in bioreactor at 20% (w/v) pulp density, 35°C with <76µm particles with biogenic Fe(III) solution {Fe(III) in feed:1g/L} against control leaching

3.2.4. Effect of temperature: Effect of temperature on bio-dissolution of uranium in the bioreactor was studied at pH 2.0 and 30% (w/v) pulp density with the mixed size particles of <76µm and results are depicted in Fig.8. The biorecovery of uranium was found to be maximum (87.6%) in 10h at 35°C as compared to 67.6% and 71.8% leaching at 25°C and 30°C respectively. Low metal leaching (76%) was observed at still higher temperature (40°C).

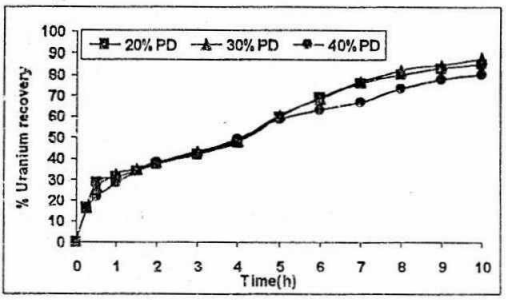

Fig.6: Uranium biorecovery at various pulp densities in bioreactor at pH 2.0, 35°C with <76µm particles

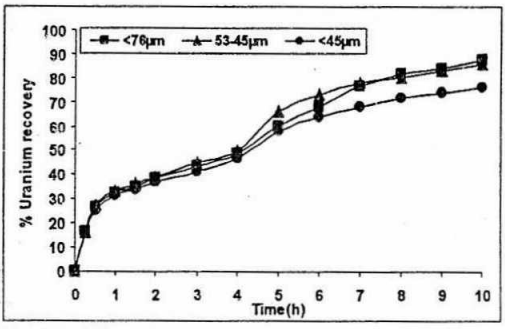

Fig.7: Uranium biorecovery at various particle sizes in bioreactor at pH 2.0, 35°C and 30% (w/v) pulp density

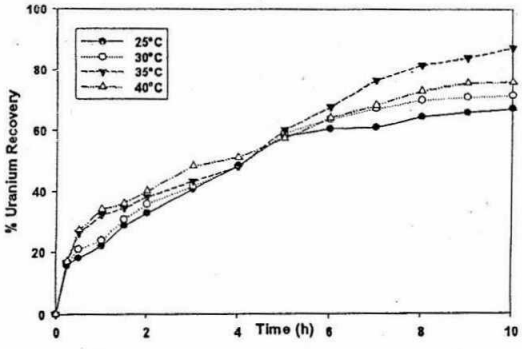

Fig.8: Uranium biorecovery at various temperatures in bioreactor at pH 2.0, 30% (w/v) pulp density with <76µm material

4. CONCLUSIONS

a) Bioleaching studies were carried out in a 2L bioreactor at 20-40% (w/v) pulp density using 10% (v/v) enriched culture of *A.ferrooxidans* and desired pH, stirring speed (150rpm) and temperature were

maintained by PLC controlled operations in the reactor.

b) With the adapted bacterial species, ~30% uranium is recovered within 1 day which increases to 74% in 12 days at the redox potential of 700mV, and finally to 98.3% with maximum redox potential of 754mV in 14 days. This shows a distinct advantage because of better mixing of slurry in the bioreactor with auto-controlled conditions that improves the kinetics. The importance of using biogenic Fe(III) in the bio-oxidation process was realized and therefore, experiments were carried out with the enriched culture of *A.ferrooxidans* containing biogenic Fe(III). An appreciable increase in bio-recovery of uranium (84.7%) at pH 2.0 with an increase in redox potential from 536–674 mV in 10h is observed as compared to the low uranium leaching (38.3%) in the control experiments with low E value (448mV) in 10h.

c) Higher uranium biorecovery (84.7%) at pH 2.0 may be attributed to the enhanced level of oxidation of U(IV) by biogenic Fe(III) initially available and produced due to bacterial oxidation.

d) The bio-recovery rises to 87.6% in 10h at pH 2.0 and 30% (w/v) pulp density with the ore particles of <76μm size as compared to 86% and 76% uranium biodissolution for 53-45μm and <45μm size materials.

e) It may thus be concluded that better permeation of lixiviant takes place with the mixed size fractions resulting in the higher metal recovery as compared to the particles of very fine size.

f) Effect of temperature on bio-dissolution of uranium indicates 87.6% recovery in 10h at 35°C as compared to 67.6% and 71.8% leaching at 25°C and 30°C respectively. Low metal leaching (76%) can be observed at still higher temperature (40°C).

ACKNOWLEDGEMENTS

We acknowledge the support given under the In-house Project of CSIR-NML, and Director, CSIR-NML for permission to publish this paper.

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