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Column bioleaching of sandstone type uranium ore deposit

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Column bioleaching has been performed on sandstone type uranium ore. The column is initially leached with H2SO4 to make the environment acidic and feasible for Thiobacillusferroxidans bacteria growth. The column later injected with acid solution containing 6g/L H2SO4, iron source 1.5g/L (Fe3+ 0.75g/L, Fe2+ 0.75g/L) and bacteria. The leaching results show that the uranium concentration increases rapidly to maximum value 445mg/L and later decreases and reduced to minimum value. Fe3+ and Fe2+ curves shows that initially Fe2+ concentration rises indicating uranium oxidation. Later raise of Fe3+ concentration shows that bacteria growing within column causing oxidation of Fe2+ ions. Flow rate decreases from 6.35ml/hr to 5.37ml/hr at the start of test but later enhance to 8.50ml/hr. Recovery curve shows that total uranium recovered in this test is 83%. Maximum recovery attained within 90 hours which later changes slightly.

Keywords: Bioleaching, uranium, Thiobacillusferroxidans, column leaching

Introduction

Bioleaching has been successfully applied to heap leaching, tank leaching and in-situ leaching of low grade ores. In early 1960s, remarkable economic benefits were achieved by carrying out bacterial in situ leaching in some mines of Lake Eliot, Canada[1], Spain[2], Russia[3] and Japan also carried out study on bioleaching and successfully applied the technology of bioleaching to the treatment of uranium, gold and copper ores and wastewater.Uranium mine in Hunan province is the earliest one in China to apply bio leaching technology. During 1965-1971, the Institute of Microbiology of the Chinese Academy of Sciences and the former five locations of nuclear industry carried out heap leaching research on surface ore with acid and bacteria[4]. In the early 1990s, the Institute of Uranium Mining of nuclear industry carried out indoor bacterial leaching experiments on uranium ore and studied the in situ bacterial leaching of low grade crushed ore of mining site.

Bioleaching is the recovery of metal from ore using single-cell microorganism[5], [6]. It is a slow process[7]–[9] and rate of bioleaching depends upon different factors like permeability of host rock, oxygen, pH, temperature, high content of pyrite in ore, uranium minerals favorable for growth and action of bacteria and presence of minerals that provide nutrition. Extraction of uranium through bacteria is due to association of uranium minerals with pyritic and sulfide mineralogy[10]. *Thiobacillusferroxidans* bacteria are considered the main source for uranium bacterial leaching.Metal (uranium) can be extracted from sulfide minerals by either direct bioleaching or indirect bioleaching [11].

In direct mechanism, *Thiobacillusferroxidans* bacteria attached physically to the surface of uranium sulfide mineral and oxidation of sulphide to sulphate takes place using intrinsic enzymes[6], [12] and results in leaching of uranium from ore but the understanding regarding initial solubilization of metal and attachment mechanism of bacteria cell are not completed. The bacteria definitely attach to crystal imperfection sites rather than attaching to the whole surface of mineral. Similarly electrochemical interaction is responsible for metal dissolution[13]–[15].

In direct mechanism oxidation of pyrite takes place. After pyrite is oxidized, sulphuric acid and ferric sulfate are produced[16]. Sulphuric acid dissolves uranium minerals containing uranyl ions. Ferric sulphate oxidizes UO_2 to UO_2^{2+}[17].

In the presence of leaching bacteria, oxygen and water, pyrite will react as follows:

$$4FeS_2 + 14O_2 + 4H_2O \xrightarrow{Bacteria} 4FeSO_4 + 4H_2SO_4 \quad (1)$$

Ferrous sulfate is oxidized to ferric sulfate:

$$4FeSO_4 + O_2 + 2H_2SO_4 \xrightarrow{Bacteria} 2Fe_2(SO_4)_3 + 2H_2O \quad (2)$$

Equation 1 & 2 can be combined to describe direct pyrite bacterial oxidation

$$4FeS_2 + 15O_2 + 2H_2O \xrightarrow{Bacteria} 2Fe_2(SO_4)_3 + 2H_2SO_4 \quad (3)$$

In indirect mechanism the bacteria cell do not physically attach to the sulfide mineral rather it produce solution which

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chemically oxidize the sulfide mineral. In acid solution, ferric ions are the solution that is produced by bacteria.

$$MeS + Fe_2(SO_4)_3 \rightarrow MeSO_4 + 2FeSO_4 + S^o \quad (4)$$

The ferrous ions produced during this reaction of sulfide mineral oxidation is utilized and re-converted/ re-oxidized into ferric ions by *Thiobacillusferroxidans* bacteria which further perform oxidation process of sulfide minerals. In indirect mechanism, *Thiobacillusferroxidans* bacteria act as catalyst to enhance the re-oxidation process of ferrous ions and convert into ferric ions. Ferrous ions oxidation by bacteria (pH 2-3) is observed to be 10^5-10^6 faster than that of chemical oxidation [18]. Sulfur produced in equation 4 may be oxidized by *Thiobacillusferroxidans* bacteria and convert into sulphuric acid (H_2SO_4). Oxidation of tetravalent uranium (insoluble) to hexavalent uranium (soluble) is an example of indirect mechanism.

$$2UO_2 + 2Fe_2(SO_4)_3 \rightarrow 2UO_2SO_4 + 4FeSO_4 \quad (5)$$

The ferric sulphate solution is considered to be produced by pyrite oxidation by *Thiobacillusferroxidans* bacteria (Eq 3). It is also observed that *T.f* bacteria produce enzymes which directly oxidize tetravalent uranium and convert into hexavalent uranium [19].

Another mechanism known as galvanic mechanism [20] in which sulphides of two different phases having different potentials come close to each other causing potential difference due to which movement of electrons take place which results in oxidation reduction process and leaching of uranium takes place at anode. *Thiobacillusferroxidans* bacteria produce sulphates by conversion of sulfur and allow dissolution at anode[21], [22].

Experimental Device and Test Conditions

Materials

The samples are drilling core samples that have been collected from the site near in situ leaching (acidic system) mining site.

Element/Mineral	Concentration	Element/Mineral	Concentration
S	0.07%	K_2O	2.69%
U	198µg/g	MgO	0.43%
Al_2O_3	12.10%	Na_2O	0.11%
CaO	0.13%	SO_3	0.18%
Fe_2O_3	1.42%	TiO_2	0.51%
Fe^{3+}	0.35%	MnO	0.01%
FeO	0.83%	P_2O_5	0.03%
SiO_2	78.48%	-	-

The detail of drilling core samples is given below in table 1.

Table 1 Core Samples Detail

Sr. No	Core Sample No.	Sampling Depth (m)	Sample Length (cm)	Lithology
1	YSC-1-K9	144.05-144.15	0.1	Grey siltstone
2	YSC-3-K-3	137.85-138.05	0.2	Light yellow medium sandstone
3	YSC-4-K-1	136.60-136.75	0.15	Grey medium sandstone
4	YSC-5-K-4	133.32-133.52	0.2	Grey pack sand
5	YSZ-1-K-5	136.09-136.39	0.3	Grey pack sand
6	YSZ-1-K-27	143.87-144.07	0.2	Light yellow coarse sand rock
7	YSZ-2-K-3	138.28-138.53	0.25	Grey pack sand
8	YSZ-2-K-8	141.14-141.34	0.2	Light yellow coarse sand rock
9	YSZ-4-K-2	134.97-135.12	0.15	Grey pack sand
10	YSZ-4-K-21	139.07-139.22	0.15	Grey medium sandstone

Table 2 shows the chemical analysis results of core sample.

Table 2 Chemical Analysis of Ore Sample

Sample Preparation and Loading

The core samples has been crushed into five different particle size range i-e>1mm, 1-0.5mm, 0.5-0.25mm, <0.25mm. 1.5g/cm^3 bulk density is used for this test and sample is weighed according to bulk density. PVC column is designed and used for this test with sample length 32cm and inner dia. 4cm. Column is loaded with sample in a way that gravels were placed at bottom with nylon mesh at its top and then sample is loaded in such a way that after every 2-3cm loading of sample, the sample is compressed with wooden cylindrical bar so that the sample is uniformly distributed within the column. After sample loading, nylon mesh is placed on sample and gravel placed above all. Valves are placed at top and bottom of column. Once sample is loaded, the column is subjected to permeability test for which tap water is injected through the column and flow rate was measured for two to three days. Average flow ratefor column is 6.15ml/hrand

permeability coefficient was determined according to Darcy'slaw $Q = \mathrm{KA}\frac{\mathrm{H}}{\mathrm{L}}$and found to be 0.020m/d.

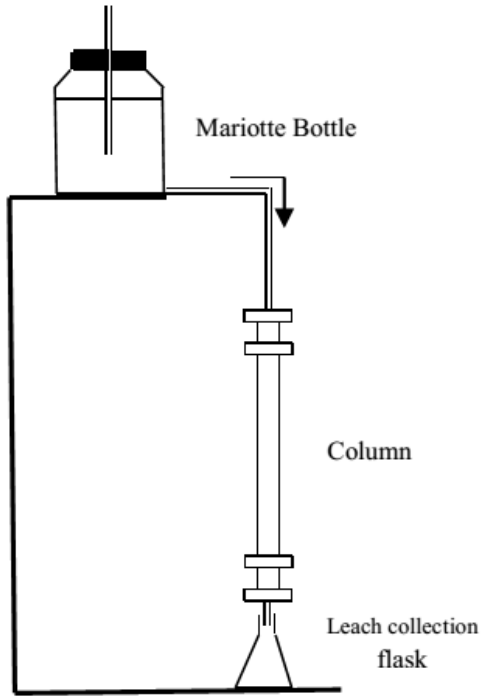


Figure 1 Test device

Test Conditions

After permeability test, column is subjected to bioleaching. Initially pH value of the column is lowered to 2 by injecting H_2SO_4 (3g/l) to make column environment feasible for bacteria growth. Once the desired pH is achieved, the column is injected with solution composed of H_2SO_4 (6g/l), Fe source (1.5g/l containing Fe^{3+} 0.75g/l, Fe^{2+} 0.75g/l) and bacteria (Thiobacillusferroxidan).

Preparation of Bacteria Medium

9K medium is used to grow bacteria. 9K medium consists of liquid A and liquid B. Liquid A consists of solution that is prepared by adding $(NH_4)_2SO_4$ (3.0g), K_2HPO_4 (0.5g), KCl (0.1g), $MgSO_4.7H_2O$ (0.5g), $Ca(NO_3)_2$ (0.01g) in 1000ml of deionized[23]. Liquid B consists of Fe^{2+} solution (50g/l) which is prepared by adding $FeSO_4.7H_2O$ (25g/l) in 200ml deionized water. H_2SO_4 is used to maintain pH 1.8.

Initially liquid A is added into flask and pH is maintained at 1.8 using H_2SO_4. High pressure sterilization of flask is done using pressure cooker for 20 minutes (T=121˚C, P=0.1MPa). After liquid A reach at room temperature, bacteria culture and liquid B is added. The flask is set in a shaking machine at 120 rpm (30˚C). After approx. 24 hours bacteria medium is prepared indicated by conversion of Fe^{2+} to Fe^{3+}. Bacteria are filtered from medium using filter paper (0.22μm) by suction pump. For each column, bacteria extracted from 500ml medium were used to ensure the efficient activity of bacteria in solution each day.

Down flow mechanism for column leaching was applied by maintaining constant head by using Marriott bottle at some height from the column and solution passes through the column by gravity. The samples collected twice a day after 12 hours. Eh and pH values were measured by using pH and Eh meter (OHAUS model: ST3100). Fe^{2+}, Fe^{3+} and ΣFe concentrations were measured by applying titration technique. Uranium content was determined by ICP-OES machine (5100 Agilent Technologies). All these content were measured simultaneously.

Results and Discussion

In this column, acidification has been done till 153hrs. From figure 2, it shows that initially Eh value falls from 247mV to 209mV whereas pH value increased from 5.96 to 7.06 after approx. 45 hours. The reason for this change is that the sample has been collected from the site that is near in-situ leaching (acidic) mining site. Therefore, the pH of sample was slightly lower than neutral.Dilution with tap water at the start of leaching test causes the pH value rise to neutral and lower the Eh value of the column. This change of pH and Eh values causes the precipitation of uranium. After approx. 50 hours pH value start decreasing and Eh value rise with time indicating the column environment becoming acidic and oxidizing. Once pH=2, the solution containing H_2SO_4 (6g/l), Fe source (1.5g/l) and bacteria injected into column. The pH value lowers to 1.5 and Ehvalue rises to 540mV with time and remains stable for rest of test.

From uranium profile, initially the uranium concentration remains minimum till 90 hours. This is due to change of pH and Eh values that take place at the early stage of test due to dilution with tap water. These changes leads to the change of the migration environment i-e causes solute (uranium) to fall into the reduction environment, and the dissolved uranium reduced/hydrolyzed and precipitated. After 90 hours, dissolution of uranium occurs and concentration of uranium rises in leach solution. The dissolution of uranium consists of two stages; in the first stage more rapid dissolution takes place which starts approximately 90 hours after solution has been injected. In second stage, dissolution slowdown gradually[24], [25]. The more dissolution in the first stage that give rise to U peak is due to the re-dissolution and accumulation of uranium in the pre hydrolyzed precipitation. With the continuous addition of the fresh solution, the reduced environment changes to the oxidizing environment, and the previously precipitated uranium re-dissolved. After 177 hours, solution containing bacteria medium and iron solution were injected. Fe^{3+} solution act as an oxidizing agent and oxidize U (IV) to soluble U (VI) which further react with acid to form soluble complexes. Fe^{3+} converted into Fe^{2+} which is utilized by the bacteria to convert them back into Fe^{3+}. Dissolution of uranium decreased gradually and reaches its minimum value after 375 hours.

Flow rate decreases initially after the injection of solution is due to the settling of fine particles and the hydrolysis of Fe^{2+},

Al and Fe^{3+} at the pH > 6, >4-5 and >3 which causes temporal plugging but the flow rate starts gradual increase as the environment become more acidic and pH decreases which causes the re-dissolution of previously precipitated of $Fe(OH)_2$, $Al(OH)_3$ and $Fe(OH)_3$. The flow rate increases drastically after 350 hours and reaches to 14.5 ml/hr.

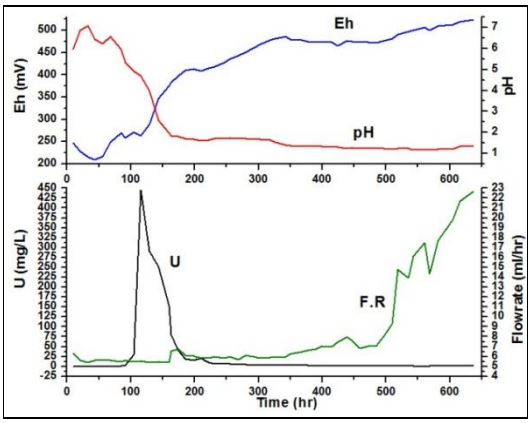
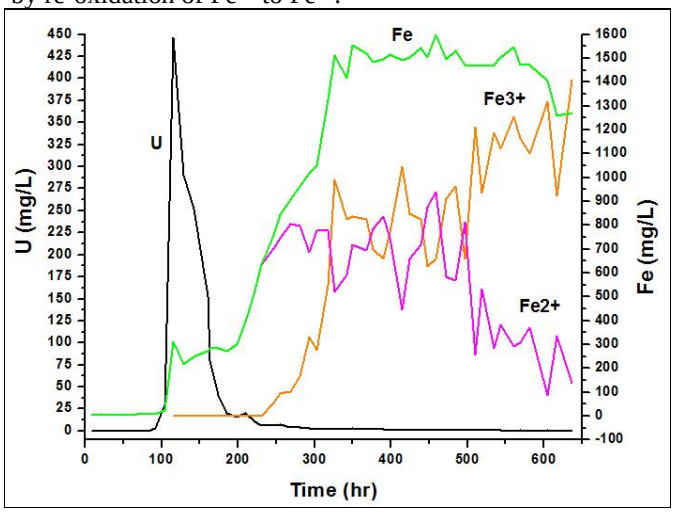


Figure 2 Relationship b/w U, flow rate, Eh, pH & t

Figure 3 shows the relationship between U, Fe^{2+}, Fe^{3+}, Fe, pH and Eh. In this figure, it shows that iron and bacteria medium (Fe^{2+} 0.75g/l, Fe^{3+} 0.75g/l) has been injected after 177 hours as pH value of the column reach 2. It can be seen that Fe^{2+} concentration increased rapidly showing that U (IV) (insoluble) is oxidized to U (VI) (soluble) form thus increasing dissolution and concentration of uranium in leach. After 300 hours, Fe^{2+} concentration starts decreasing on the other hand concentration of Fe^{3+} start increasing which shows that bacteria are growing in the column causing re-oxidation of Fe^{2+} and increasing the concentration of Fe^{3+} ion which eventually give rise to Eh value. Thus bacteria activity increases the Eh value

by re-oxidation of Fe^{2+} to Fe^{3+}.



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Relationship b/w U, Fe^{3+}, Fe^{2+}, Fe & t

Figure 4 shows relationship of recovery, pH and Eh. In this figure it is shown that maximum recovery is done from 110 hours to 200 hours i-e within 90 hours and the pH value changes from weak acid to strong acid and Eh value changes from reducing to oxidation environment. U recovery reaches to its maximum value i-e 83% at the end of leaching process.

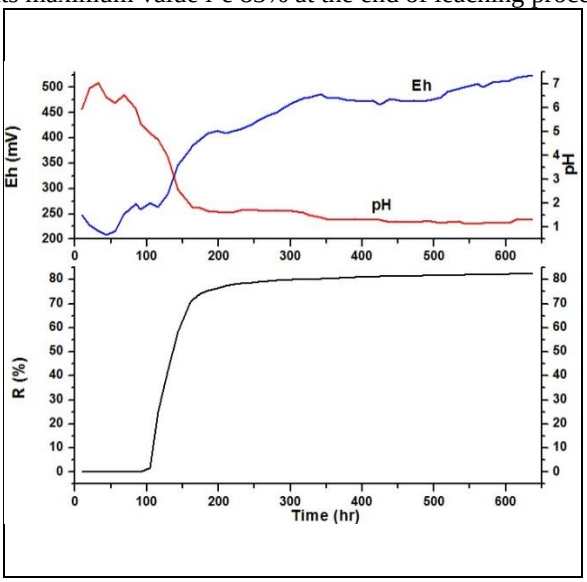

Figure 4 Recovery curve

Conclusions

The results from this study shows that the dissolved uranium profile of bioleaching column follow a trend in which uranium concentration changes from low to high to maximum value 450mg/L and then reduced and remain constant at low value. During initial stage of test, rise of pH value and decline of Eh value is due to the reason that the sample has been collected from site that is near to in-situ leachiong (acidic) project due to which sample become acidic and therefore pH is slightly lower than neutral. During initial leaching with tap water, dilution takes place due to which pH value increased and Eh value fall. Due to these changes, uranium hydrolyzed and precipitation take place.Re-dissolution of previously precipitated uranium occurs as fresh solution is supplied continously and give rise to maximum uranium peak on uranium profile.Fe^{3+} and Fe^{2+} profile shows that initial rise of Fe^{2+} concentration shows that oxidation of U takes place and Fe^{3+} is converted to Fe^{2+} but later Fe^{3+} concentration rises which indicates that bacteria are growing with in the column and re-oxidation of Fe^{2+} to Fe^{3+} is taking place hence rising the Eh value of the column. The flow rate curve shows the initial decline which is due to fine particle migration and temporary plugging caused by metal (iron,aluminium)hydroxides at relatively higher pH value. Removal of temporary plugging at low pH causes the flow

rate to enhance at later stage. Recovery curve shows that maximum recovery of uranium take place within 90 hours which later changes very slightly with time. 83% uranium recovered in this column bioleaching test.

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References

[1] K. Hu, "Bioleaching of uranium," *Uranium Min.*, vol. 1, pp. 14–29, 1991.
[2] T. A. Munoz and Ballester, "A study of bioleaching of Spanish ore," *Hydrometallurgy*, vol. 38(1), pp. 39–97, 1995.
[3] J. Liu and R. Qiu, "Preparation technology of underground bacterial leaching solution," *World Min. Express*, vol. 11, no. 19–22, 1992.
[4] F. X. Xiao, "Feasibility exploration of changing retention leaching mining method to 320 uranium deposit," *Uranium Min.*, vol. 1, pp. 7–11, 1990.
[5] J. Barret, M. Hughes, G. Karavaiko, and P. Spencer, *Metal extraction by bacterial oxidation of metals*. London: Horwood, 1993.
[6] K. Dwivedy and A. Mathur, "Bioleaching-our experience," *Hydrometallurgy*, vol. 38, pp. 99–109, 1995.
[7] G. E. Livesey, "An Oscar for bacteria," *Nucl Act.*, vol. 20, pp. 8–11, 1980.
[8] T. A. Munoz, F. Gonzalez, M. L. Blazquez, and A. Ballester, "A study of the bioleaching of a Spanish uranium ore, Part I: a review of bacterial leaching in the treatment of uranium ores," *Hydrometallurgy*, vol. 38, pp. 39–57, 1995.
[9] G. Rossi, *Biohydrometallurgy*. New York: McGraw Hill, 1990.
[10] J. W. Clegg and D. D. Foley, *Uranium ore processing*. Boston: Addison Wesley Publishing, 1958.
[11] M. P. Silverman and H. L. Ehrlich, *Microbial formation and degradation of minerals*, vol. 6. New York: Academic Press, Inc., 1964.
[12] K. A. Natrajan, "Microbiological applications and techniques in biogeochemistry," in *Interantional Workshop Environ. Biogeochem.*, 1998, pp. 59–79.
[13] M. Rodriguez-Leiva and H. Tributsch, "Morphology of bacterial leaching patterns by Thiobacillus ferrooxidans on synthetic pyrite," *Arch. Microbiol.*, vol. 149, no. 401–405, 1988.
[14] H. L. Ehrlich, *Geomicrobiology*. New York: Marcel Dekker, 1996.
[15] J. C. Bennet and H. Tributsch, "Bacterial leaching patterns on pyrite crystal surfaces," *J. Bacteriol.*, vol. 134, pp. 310–317, 1978.
[16] M. P. Silverman, "Mechanism of bacterial pyrite oxidation," *J. Bacteriol.*, vol. 94, pp. 1046–1051, 1967.
[17] K. Hu, S. Y. Huang, J. H. Yang, and C. Y. LI, "Bioleaching of uranium from ore in Hunnan," *Hydrometall. China*, vol. 2, pp. 85–88, 2003.
[18] D. T. Lacey and F. Lawson, "Kinetics of the liquid phase oxidation of acid ferrous sulfate by the bacterium Thiobacillus ferrooxidans," *Biotechnol. Bioeng.*, vol. 12, pp. 29–50, 1970.
[19] A. A. Di Spirito and O. H. Tuovinen, "Uraneous ion oxidation and carbon dioxide fixation by Thiobacillus ferroxidans," *Arch. Microbiol.*, vol. 133, pp. 28–32, 1982.
[20] S. M. Jonathan and J. J. Mark, *Uranium processing and properties*. New York: Springer, 2013.
[21] T. A. Munoz, F. Gonzalez, M. L. Blazquez, and A. Ballester, "A study of the bioleaching of a Spanish uranium ore, Part II: orbital shaker experiments," *Hydrometallurgy*, vol. 38, pp. 59–78, 1995.
[22] R. McCready, D. Wadden, and A. Marchbank, "Nutrient requirements for the in place leaching of uranium by Thiobacillus ferroxidans," *Hydrometallurgy*, vol. 17, pp. 61–71, 1986.
[23] Y. J. Wang, Z. Zheng, P. G. Zhou, Y. Zhong, and X. C. Peng, "Study on growth of Thiobacillus ferroxidan and precipitates in different mediums," *Biotechnology*, vol. 16 (4), pp. 70–73, 2006.
[24] F. Brandt, D. Bosbach, E. Krawczyk-Barch, D. Arnold, and G. Bernhard, "Chlorite dissolution in the acid pH-range: a combined microscopic and macroscopic approach," *Geochim. Cosmochim. Acta*, vol. 67, no. 1451–1461, 2003.
[25] S. L. Brantley, "Kinetics of mineral dissolution," in *Kinetics of Water-Rock Interaction*, 2008, pp. 151–210.