

Column Bioleaching of Fluorine-Bearing Uranium Ore

Xiaolan Mo^a, Xiang Li^b, Jiankang Wen^c, Liulu Cai^d

National Engineering Laboratory of Biohydrometallurgy, General Research Institute for Nonferrous Metals, Beijing 100088

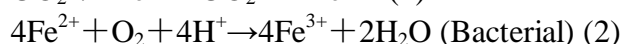
^ae-mail: mxl0545@163.com, ^be-mail: kw0702lx@163.com, ^ce-mail: kang3412@126.com, ^de-mail: cailiulu_03@163.com

Keywords: Uranium bioleaching; fluorine toxicity; MLA; pitchblende; column leaching

Abstract. The results of MLA automated quantitative mineralogy system indicated the uranium ore used in this study was mainly composed by pitchblende (0.467%), quartz (64.911%), fluorite (2.177%) and pyrite (0.436%). High content fluorite and low content pyrite mineral were unfavorable for extracting of uranium by bioleaching; furthermore, the relatively higher U⁴⁺ in this uranium ore resulted it is difficult to dissolve with sulfuric acid. The fluoride-tolerance mixed microbes (*Acidithiobacillus ferrivoran*, *Acidithiobacillus ferrooxidans*, and *Leptospirillum ferriphilum*) were used for bioleaching of uranium, and the bacterial leaching and acid leaching experiments of fluoride-containing uranium ore were investigated in column during 38 days. The experiment with mixed culture and added ferrous reached the highest uranium recovery rate (72.04%), which exceeded the recovery rate of traditional acid leaching technique 12%. High uranium recovery was founded to be due to the addition ferrous iron that can be readily achieved by fluoride-tolerance bacterial leaching. The results of this paper will lay the foundation for high fluoride uranium biological heap leaching tests.

Introduction

Uranium is found in a great variety of ores, of which only a few are of any economic importance. Among these are uraninite and pitchblende, which represent different crystalline forms of UO₂ in vein deposits [1]. Sulfuric acid is the most common leaching agent used in the extraction of uranium. Uranium usually presented in ores in tetravalent state U⁴⁺, which must be oxidized to hexavalent state U⁶⁺ before it can be dissolved in sulfuric acid solution. In acid leaching, the uranium oxidation reaction requires the presence of ferric ion, as follows equation [2, 3].



Fe²⁺ produced in reaction (1) must be re-oxidized to Fe³⁺ in reaction (2) and recycled by bacterial action. In the process of uranium leaching from low-grade uranium ore, the insoluble U⁴⁺ in the ore can be oxide into easily leached U⁶⁺ by adding proper amount of oxidant. The capacity of the microorganisms which take part in these transformations, principally bacteria of the genus *Acidithiobacillus* sp. and *Leptospirillum* sp., etc., to grow in highly acidic environment with high heavy metal content [4-6]. The bioleaching of a low-grade uranium ore using natural, pure, and mixed cultures of *A. ferrooxidans* and *Acidithiobacillus thiooxidans* (*A. thiooxidans*) has been studied in this process, the best of uranium recovery results were obtained with the mixed culture [7]. Various oxidants such as Fe₂(SO₄)₃, MnO₂, NaClO₃, H₂O₂ etc. are widely employed as a ferrous ion oxidant in uranium leaching processing [8]. Although the bio-oxidation is about 10⁵-10⁶ times faster than the chemical oxidation [9]. Besides, the existence of fluorine-containing minerals plays a strong inhibition role of bacterial activity in the bioleaching process [10-13], which was a bottleneck of bioleaching technique applied in high fluorine content uranium ore. In the leaching process, the F⁻ was combined with heavy metal ions such as Al³⁺, Fe³⁺ and Mn²⁺ to generate some complex compounds, and reduced its toxicity [14], so that it makes possible for bacteria to tolerate and grow in a high fluorine concentration [15].

Materials and methods

Materials. Uranium ores from a deposit (Guangdong, China) were used. The ore was crushed to -8mm. A series of column tests was performed using 330 kg ore which were crushed to -6mm. A representative sample was prepared by coning and quartering ground to -0.074mm for chemical analysis. The mineralogical composition was analyzed by MLA (Mineral Liberation Analyser) automated quantitative mineralogy system.

Column leaching. The columns, 30 cm in diameter and 200 cm high, made with polyvinyl chloride (PVC). Layers of cobblestones in nylon net were covered at the bottom in order to enhance the permeability of leaching solution, which supported the ore sample. The drip irrigation liquid was introduced through a feed solution tank at the top of the column, and another leachate solution tank beside the base of column was used to collect leachate solution. Initially, the uranium ore was leached by sulfuric acids liquid ($5\text{-}30\text{ g}\cdot\text{L}^{-1}$), and then the leaching residue was leached by bacterial liquid in 1# and 3# column. As comparison to the results from the 1# (6mm) and 3# (6mm) column leaching, the uranium ore was leached by sulfuric acids liquid in 2# (8mm) and 4# (8mm) column (control group). The liquid-solid ratio of each column was similar (about 4.5), and the irrigation liquid was placed high for dripping leaching. The irrigation frequency was 12h/d, the irrigation intensity was $10\text{-}15\text{ L}/(\text{h}\cdot\text{m}^2)$, and was not continuous. The 38 days column leaching process included 19days acid pre-leaching stage and 19 days bioleaching stage. After the leaching study, the contents of uranium in the leachate were determined by chemical microtitration with reduction of ammonium vanadate by titanous chloride. Sample volumes of liquid were extracted and the pH and redox potential (Eh) were measured.

Bacteria and its cultivation. The microorganisms used in the bioleaching study was isolated from the acid mine drainages (AMD) sample of the uranium deposits in the National Engineering Laboratory of Biohydrometallurgy, the principally compositions of microbial population were *A. ferrivorans* (33.3%), *A. ferrooxidans* (56.8%), and *L. ferriphilum* (8.5%), and others (1.4%). The tolerance of mixed culture to fluoride can reach concentrations of up to $3\text{ g}\cdot\text{L}^{-1}$. The inoculum was cultivated in an aeration culture tank. Culture medium: ferrous sulfate was added to the mine water and tailing water as the energy resource for the microorganisms (ferrous concentration of 4.5 g/L). Parameter conditions of aeration culture: time 24h, temperature 33°C , pH 2.0-2.5, and aeration intensity $2.0\text{-}3.0\text{ m}^3/(\text{m}^2\cdot\text{h})$. To the bacterial culture of mature period (bacterial solution with 5.0 g/L Fe^{3+}), the pH value was adjusted to 1.70 using 50% H_2SO_4 , as drip irrigation liquid in column bioleaching test.

Results and discussion

Mineralogical analysis. The MLA analysis results of raw minerals are shown in Table 1. It was found that the uranium minerals is mainly composed by pitchblende (0.467%), coffinite (0.028%) and brannerite (0.004%), and gangue minerals are mainly consisted of quartz (64.911%), orthoclase (10.881%), biotite (9.418%), albite (4.015%), calcite (3.705%), fluorite (2.177%), muscovite (1.677%), pyrite (0.436%) and dolomite (0.391%), etc.. Pitchblende, the principal uranium ore, has the ideal composition UO_2 .

Table 1 Mineralogical composition of ore

Minerals	Content /%	Minerals	Content /%	Minerals	Content /%
Coffinite	0.028	Dolomite	0.391	Kaoline	0.026
Pitchblende	0.467	Muscovite	1.677	Rutile	0.075
Brannerite	0.004	Biotite	9.418	Other	0.261
Thorite	0.003	Albite	4.015	Quartz	64.911
Pyrite	0.436	Orthoclase	10.881	Fluorite	2.177
Galena	0.040	Anorthite	0.175	Apatite	0.019
Hematite	0.617	Hedenbergite	0.568	Garnet	0.026
Calcite	3.705	Wollstonite	0.079	Total	100

The chemical characteristics are shown in Table 2. Although, pitchblende is always partially oxidized, with the U^{4+} converted to U^{6+} , this ore sample degree of oxidation only reach 20%. The sample of uranium ore contained 0.22% U. The U^{4+} is difficult to dissolve with sulfuric acid. The

beneficial and harmful minerals for the bioleaching are pyrite and fluorite respectively, but the content of pyrite is low. Therefore, the ore belongs to the hardly leached uranium ore.

Table 2 Chemical composition of raw uranium ore sample (Mass fraction, %)

Element	Ca	Mg	Al	Fe	K	Na	Mn	S	SiO ₂	Ti	P	U ⁴⁺	U ⁶⁺
Content	3.26	0.36	3.9	1.09	2.27	0.12	0.079	0.53	76.48	0.12	0.012	0.18	0.04

Column of leaching test. The leaching solution Eh values of the column inlet and outlet are shown in Fig.1. Before getting into the column, the initial Eh value of the solution was greater than 500mV; however, it was lower than 320mV at outlet, which is due to the increase of the ferrous ion in the solution. When the acid consumption approaches equilibrium, the Eh value of the solution also changed less than before. In the second stage of leaching, because the initial Eh value of the leaching solution with bacteria was higher, the initial Eh value of 1# and 3#column feed liquor was about 100mV higher than that of 2# and 4# column. The changes of Eh values reflect the different leaching conditions of each column well. These results indicated the higher redox potential of ore leaching solution, the better oxidation leaching effect of uranium. The high redox potential played a key role in accelerating uranium dissolution in the bioleaching stage.

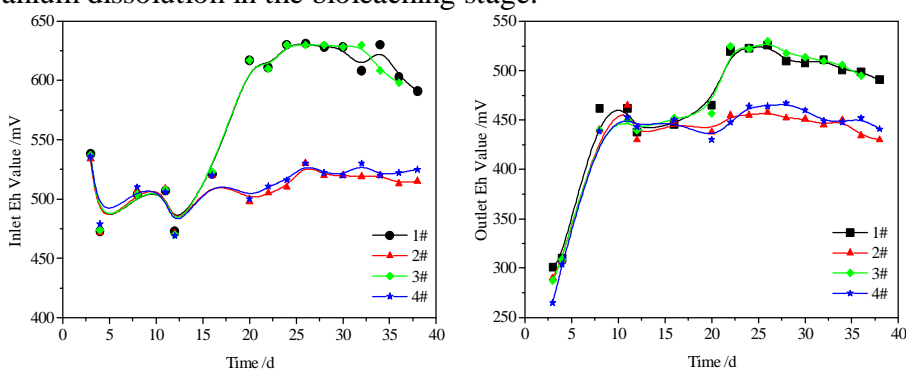


Fig. 1. Variation of Eh of leach solution with time

By measuring the change of the concentration of uranium in the leaching solution, the leaching rate of each column is calculated and shown in Fig. 2. The uranium leaching rate of 1#, 2#, 3#, 4# column reached 72.04%, 65.42%, 61.61% and 55.07% respectively after a 38-day leaching. The uranium leaching rate of 1# and 3# column had significant improvement because bacterial culture fluid was used as leaching solution in the latter stage of the leaching process, and it has been increased by approximately 10%-12%.

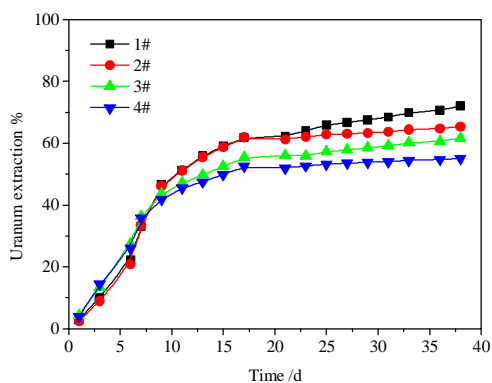


Fig. 2. Variation of leaching rate of uranium with time in different column

Conclusions

The ore was mainly composed by pitchblende, quartz, fluorite and pyrite, etc.; high content fluorite and low content pyrite mineral were unfavorable for extracting uranium by bioleaching. By the indirect mechanism, it is necessary to improve uranium ore bioleaching by addition of Fe²⁺. The Fe²⁺ can be re-oxidized to Fe³⁺ by bacteria, and the Fe²⁺ can be regenerated by the leaching process. In 38 days, the experiment with mixed culture and added ferrous reached the highest uranium recovery rate (72.04%),

which exceeded the recovery rate of traditional acid leaching technique 12%. The value of redox potential (Eh) in bioleaching were over 500mV, increased about 100 mV as compared with the acid leaching, and enhanced effectively the oxidizing atmosphere, thus promoted the oxidation leaching of reduction state uranium (U^{4+}). The leaching rate of uranium by using the particle size (-8mm) was significantly lower than that of by using the particle size (-6mm). Therefore, to get a better bioleaching effect, the crushing process of existing ore needs to be modified. The experimental study in this paper will laid the foundation for the biological heap leaching test of fluorine-containing uranium ore.

Acknowledgments

This study was financially supported by the National Natural Science Foundation of China (No.51404031) and the National High Technology Research and Development Program of China (No.2012AA061501).

References

- [1] J.A. Muñoz, F. González, M.L. Bliáquez, A. Ballester. *Hydrometallurgy*. Vol. 38 (1995), p.37.
- [2] A. Rashidi, J. Safdari, R. RoostaAzad, S. Zokaei-Kadijani. *Annals of Nuclear Energy*. Vol. 43 (2012), p.13.
- [3] S. Singh, K.D. Mehta, V. Kumar, B.D. Pandey, V.M. Pandey. *Hydrometallurgy*. Vol. 95 (2009), p. 70.
- [4] M. Eisapour, A. Keshtkar, M.A. Moosavian, A. Rashidi. *Annals of Nuclear Energy*. Vol. 54 (2013), p. 245.
- [5] S. Pal, D. Pradhan, T. Das, L. Sukla, G.R. Chaudnury. *Indian Journal of Microbiology*. Vol. 50 (2010), p.70.
- [6] B.C. Patel, D.R. Tipre, S.R. Dave. *Bioresource Technology*. Vol. 118 (2012), p. 483.
- [7] A.B. Umanskii, A.M. Klyushnikov. *J. Radioanal. Nucl. Chem.*. Vol. 295 (2013), p. 151.
- [8] C. R. Edwards. *JOM*. Vol. 52 (2000), p. 12.
- [9] K.D. Mehta, V. Kumar, B.D. Pandey, P.K.Tamrakar. *Energy procedia*, Vol. 7 (2011), p. 158.
- [10] X.L. Mo, J.K. Wen, C.Y. Xu, B. Wu, B.W. Chen, H. Shang. *Advanced Materials Research*. Vol.1130 (2015), p. 468.
- [11] I. Suzuki, D. Lee, B. Mackay, L. Harahuc, J.K. Oh. *Appl Environ Microbiol*. Vol. 65 (1999), p. 163.
- [12] M. Dopson, A. Halinen, N. Rahunen, D. Bostrom, J.E. Sundkvist, M.R. Vanhanen, A.H. Kaksonen, J.A. Puhakka. *Biotechnology and Bioengineering*. Vol.99 (2008), p. 811.
- [13] J.A. Brierley, M.C. Kuhn. *Advanced Materials Research*. Vol. 71(2009), p. 311.
- [14] T.C. Veloso, L.C. Sicupira, I.C.B. Rodrigues, L.A.M. Silva, V.A. Leão. *Biochemical Engineering Journal*. Vol. 62 (2012), p. 48.
- [15] X.L. Mo, J.K. Wen, B.W. Chen, M.L. Wu, W.C. Gao. *Chinese Journal of Rare Metals*. Vol. 39 (2015), p. 75.