

Bioleaching of fluoride-containing uranium: flask experiments with fluoride-resistant bacteria

Xiang Li^{1,a}, Xiaolan Mo^{1,b}, Jiankang Wen^{1,c}, Biao Wu^{1,d}, Diansuo Wang^{1,e}, Hongying Yang^{2,f}

¹National Engineering Laboratory of Biohydrometallurgy, General Research Institute for Nonferrous Metals, Beijing 100088, China

²School of metallurgy, Northeastern University, Shenyang 110891, China

^ae-mail: kw0702lx@163.com, ^be-mail: mxl0545@163.com, ^ce-mail: kang3412@126.com, ^de-mail: angelwbiao@sina.com, ^ee-mail: wu_ml_7483@163.com, ^fe-mail: yanghy@smm.neu.edu.cn

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Abstract. The results of MLA automated quantitative mineralogy system indicated the uranium ore used in this study was mainly composed of pitchblende(1.026), aluminosilicate(include biotite(31.72%), albite(13.98%) and orthoclase(13.43%)), and fluorite(0.94%). The fluoride-resistant bacteria strain could growth normally under the condition of fluoride ion concentration as high as 600mg/L. The uranium extration rate of bioleaching flask reached 74% in 10 days, bioleaching have obvious advantages compare to conventional acid leaching (46%).

Introduction

Utilizing of low grade uranium ores is a great challenge with the depletion of high-grade uranium ores and the increasing demand of nuclear energy for uranium material[1,2]. Bioleaching is a well-established technology and an alternative to conventional pyrometallurgical processes for the treatment of uranium[3,4]. It has many advantages such as adaptation to low-grade ores, short leaching cycle, relatively low cost and low contamination. For the fluoride-containing uranium, the application of bioleaching was limited. As a strong hydrogen bonding species, fluorid could enter into the cell by species of HF and affect bacterial metabolism[5]. Therefore, the microbiological shake flask test was selected to test the domestication effect of fluoride-resistant bacteria. Explored the test cycle, acid consumption and leaching rate to provide scientific basis for the mining of fluorine-containing uranium ore, and to provide process parameters for industrial heap leaching production.

Materials and methods

Ore samples. Bioleaching experiments were carried out with the uranium ore samples, the chemical analyses of these are listed in Table 1.

Table 1: Chemical analysis (%) of the ore samples studied

Si	Al	Fe	Ca	Ti	K	Zr	Mg	S
30.7	9.38	3.434	2.1	0.375	3.34	0.023	0.772	0.382
Na	Mn	P	Mo	Th	Y	F	U	Sr
0.361	0.055	0.293	0.114	0.079	0.022	0.516	0.234	0.021

A mineralogical analysis was previously performed using MLA and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) (table 2). The mainly uranium-contained minerals were pitchblende (1.026%), brannerite (0.314%), coffinite (0.070%); Other mainly sulfides metal were pyrite (1.454%) and a small amount of galena, sphalerite, arsenopyrite, etc ; Mainly oxides metal was hematite (0.140%); Non-metallic gangue minerals were accounted for more than 90% of the ore samples. Mainly gangue minerals were biotite (31.757%) and quartz (27.724%), followed by

albite (13.975%) and orthoclase (13.425%). Alkaluminite minerals were account for more than 64% of the ore samples.

Table 2 Mineral composition and relative content of the uranium ore

Mineral	Wt%	Mineral	Wt%
Coffinite	0.070	Biotite	31.757
Pitchblende	1.026	Albite	13.975
Brannerite	0.314	Orthoclase	13.425
Thorite	0.132	Anorthite	0.160
Pyrite	1.454	Hedenbergite	0.087
Galena	0.101	Apatite	1.595
Hematite	0.140	Garnet	0.291
Quartz	27.724	Wollstonite	0.005
Fluorite	0.940	Kaoline	0.018
Calcite	1.280	Rutile	0.177
Dolomite	0.241	Other	0.097

Bacteria. The fluorine-tolerance bacteria used in this study were obtained from National Engineering Laboratory of Biohydrometallurgy (China), named NFCJ-6 strains, composed of *At. ferrooxidans* and *Acidiphilium sp.* Bacterial growth was carried out in the 9K medium (3 g/L $(\text{NH}_4)_2\text{SO}_4$, 0.5 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 g/L K_2HPO_4 , 0.1 g/L KCl, 0.01 g/L $\text{Ca}(\text{NO}_3)_2$ and 44.2 g/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

Bioleaching experiments. The fluoride-containing uranium leaching experiments were carried out in 250 ml conical flask, shake flasks in a temperature-controlled incubator that was held at $30 \pm 1^\circ\text{C}$, 160 rpm. Two sets of shake flask tests were set up, one for microbial leaching and the other one for acid leaching. The leaching system is 80 mL of iron-free 9K medium with a liquid to solid ratio of 4:1 (80 mL of solution: 20 g of ore). Bioleaching flasks was inoculated in the 6th day of testing with the fluoride-resistant strain. the pregnant leach solution (PLS) collected of each flask had liquor aliquots withdrawn for subsequent analyses (i.e. measurement of the pH, Eh, bacterial counts and analysis of the elements concentration). Subsequently, the PLS volume was recorded and this was then used in uranium extraction calculations. Analyses and evaporation losses were compensated with distilled water. After the pH was adjusted with dilute H_2SO_4 (H_2SO_4 : H_2O =1:1).

Results and discussion

Profile of pH and acid consumption. One of the key parameters in bioleaching operations is the pH of the solution. Whilst higher acidities are important for mineral dissolution, the pH must be set at values that simultaneously ensure an optimum bacterial growth rate and high concentrations of ferric iron in solution.

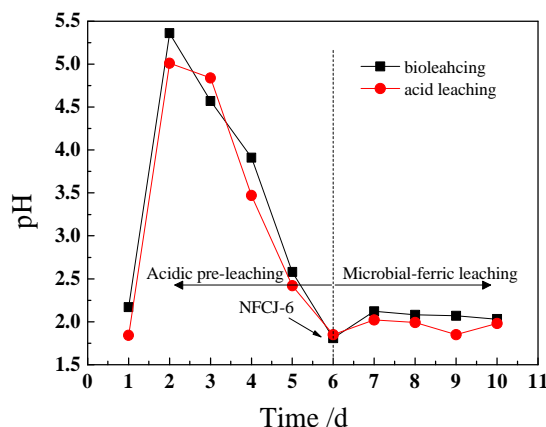


Fig.1 The pH dynamic variation in the leaching solution during leaching of uranium

The pH value of 2.00 ± 0.05 was selected in this study, because of above a pH of 2.5, the ferric iron will forms in jarosite precipitation and lose the oxidation activity. As shown in Fig.1, after the acidification of the ore in the column with a dilute sulfuric acid solution for 6 days, the pH was reduced to about 2.0, which created the best conditions for subsequent microbial leaching. In the 6-day pre-soaking stage, the sulphuric acid consumption reached 62.02 kg/t ore(bioleaching) and 64.00 kg/t ore(acid leaching).

Dissolution of gangue elements. Gangue minerals, in addition to acid consumption, account for the presence of elements in the leachate, that may affect bacterial growth, dependent on nature and concentrations of those elements. Thus, from a metallurgical and bacterial viewpoint, the profile of the most critical species must be assessed. Aluminum- and fluoride-bearing minerals were detected during mineral characterization and the content of these in both samples was fairly high (Tab.1). The anion is harmful to acidophilic bacteria and the presence of both in the leachate was due to the solubility of fluorite and apatite in acidic media. In the first 6 days of leaching, aqueous fluoride concentrations were mostly exceed 600 mg/L(Fig.2), which were significantly impair ferrous iron bio-oxidation. This is a very high concentration, given the low fluoride tolerance reported for *At. ferrooxidans*, i.e. bacterial growth was shown to be severely hampered for concentrations above 20 mg/L fluoride [6]. In bioleaching system, after adding the NFCJ-6 strain, the concentration of F^- in the solution dropped significantly, and the concentration of F^- in the solution dropped to 450 mg/L after 1 day. After 3 days, the concentration of F^- in the solution was almost undetectable. It is due to the fact that Fe^{3+} produced by bacterial growth completely complex with F^- in the solution. The results showed that the fluoride-resistant strains had obvious effects on fluoride tolerance, and the bacteria still had high iron oxidizing ability in the high-fluorine environment. In the acid leaching test, after 6 days of acidic leaching, the concentration of F^- in the solution also showed a tendency to decrease, but the amplitude was smaller and only decreased less than 100 mg/L. It is because that the aluminosilicate gangue minerals slightly dissolve out of Al^{3+} during the leaching process and complex a portion of the F^- , resulting in a decrease of the concentration of F^- .

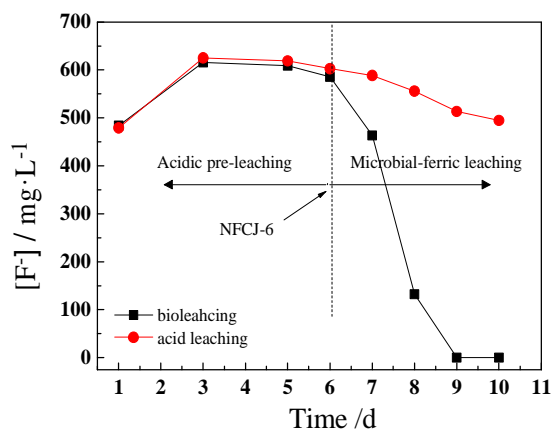


Fig.2 The variation of F^- during leaching of uranium

Solution potential and iron profile. The solution potential is affected by ferric iron produced by the bacteria and is therefore related to the bacterial population present in the system.

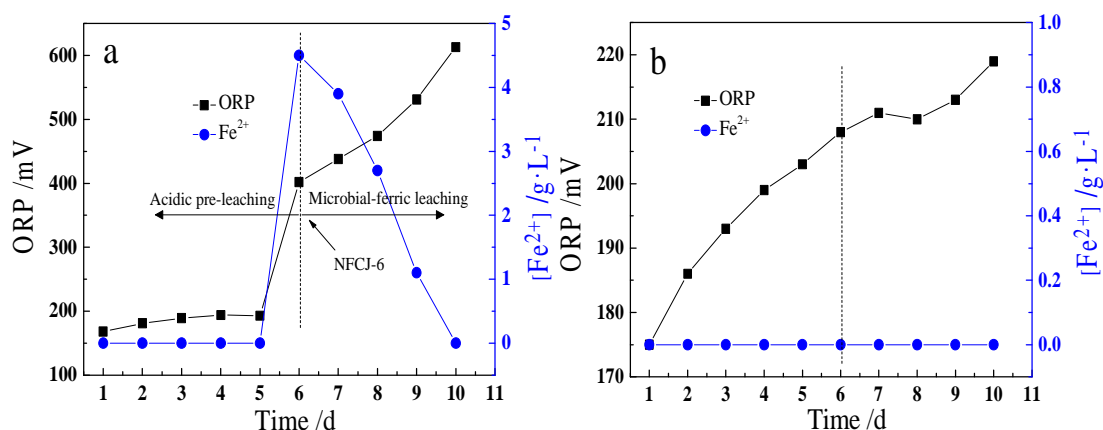


Fig.3 The variation of Eh and iron concentration in leaching process (a: bioleaching; B: acid leaching)

This can be seen in Fig. 3 which shows significantly higher Eh values in all of the inoculated flask as compared to the non-inoculated tests. In the context of bioleaching, the solution potential is defined by the activities of ferrous and ferric iron in the leachate; thus, the Fe^{2+} concentration profile is shown in Figure 1(c). The inoculated columns demonstrated higher concentrations of soluble iron (4 g/L) than it detected in the non-inoculated flask.

Uranium extractions. Despite the high fluoride concentrations depicted in Fig.3, uranium dissolution was slow and leaching rate can be achieved 40% around (both bioleaching flask and acid leaching flask) at the acidic pre-leaching stage. At later acidic pre-leaching stage, the dynamic of uranium leaching was insufficient, as the leaching rate of 5th and 6th were similar. After leaching for 10 days, the leaching rate of uranium ore by biological leaching was 74.71%, while that by acid leaching was only 46.61%. The test results show that the leaching rate of leaching uranium by microbial leaching is increased by 28.1%.

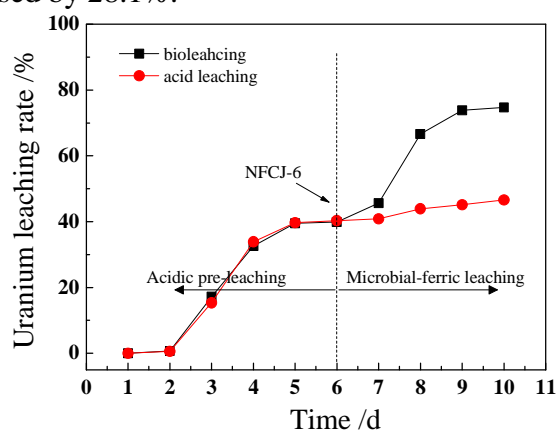


Fig.4 The variation of uranium leaching rate in leaching process

Conclusions

Through the experiment, the domestication effect of fluoride-resistant bacteria was verified, and it can still work normally under the condition of fluoride ion concentration as high as 600mg/L. compared to acid leaching, the uranium extraction rate in the bioleaching can reach 74.71%, which exceeded more than 28%.

Acknowledgements

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References

- [1] Y.Q. Cai, J.D. Zhang, Z.Y. Li, et al. Outline of uranium resources characteristics and metallogenetic regularity in China. *Acta Geologica Sinica*, Vol.6 (2015), p.1051
- [2] A. Mishra, N Pradhan, R.N. Kar, et al. Microbial recovery of uranium using native fungal strains. *Hydrometallurgy*, Vol. 1-2 (2009), p. 175
- [3] Y.D. Wang, G.Y. Li, D.X. Ding, et al. Factors influencing leaching of uranium ore by organic acids from *Aspergillus niger*. *CIESC Journal*, Vol. 5 (2012), p.1584
- [4] L.Y. Ma, X.J. Wang, J.M. Tao, et al. Differential fluoride tolerance between sulfur- and ferrous iron-grown *Acidithiobacillus ferrooxidans* and its mechanism analysis. *Biochemical Engineering Journal*, (2017), p.59
- [5] L. Guneriusson, Å. Sandstrom, A. Holmgren, et al. Jarosite inclusion of fluoride and its potential significance to bioleaching of sulphide minerals. *Hydrometallurgy*, Vol. 1-2 (2009), p.108
- [6] M. Dopson, A.K. Halinen, N. Rahunen, et al. Silicate mineral dissolution during heap bioleaching, *Biotechnol. Bioeng*, Vol. 99 (2008), p.811