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Leaching of nickel-molybdenum sulfide ore in membrane biological reactor

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Abstract: The bioleaching of molybdenum from its sulfide ore using a Mo-resistant thermophilic bacterium *sulfolobus metallics* combined with a membrane biological reactor (MBR) was studied. The experimental results showed that the concentration of Mo can be controlled by filter of the membrane in MBR and the toxicity of Mo to microorganism is decreased in the process of bioleaching. It was also evidenced that there were different leaching rates of Ni and Mo when the concentration of Mo was different. After leaching for 20 d in the MBR at Mo concentration of 395 mg/L, the leaching rates of Ni and Mo reached the maximum of 79.57% and 56.23% respectively under the conditions of 100 g/L of mineral density, 65 °C, pH=2 and 1.0 L/min of the aeration rate. While 75.59% Ni and 54.33% Mo were leached out in column without membrane under the same conditions.

Key words: membrance biological reactor; nickel-molybdenum sulfide ore; sulfolobus metallics; bioleaching; molybdenum toxicity

1 Introduction

Molybdenum (Mo) is an important element in modern industry. Traditionally, Mo is extracted from its ore by the combination of pyro- and hydro-metallurgies. In recent years, bioleaching has become the flagship due to its great potential in simplicity and eco-friendly operation. However, the application of bioleaching is confronted with the low extraction efficiency by current technology [1]. A lot of investigations [2−5] have been performed on extracting Mo from low-grade Mo sulfide ore with the *Mesophile*, but ended up for very low leaching rates of Mo and relatively long leaching cycle. TONG [6] and DONATI et al [7] used *Acidithiobacillus ferrooxidans* to leach the low-grade sulfide ore containing Cu and Mo, and the leaching rates of 60% for Cu but only 0.34% for Mo were obtained at 30 °C. There exist several reasons for the aforementioned phenomenon. It was discovered that *Acidithiobacillus ferrooxidans* did not absorb on hydrophobic MoS_3, which may inhibit the efficiency of direct bioleaching. More importantly, the presence of a low concentration of extracted Mo in the solution has toxic effect on the biological activity of the microbes. The experiment done by SILVERMAN and LUNDGREN [8] showed that 1 mmol/L Mo in 9 K medium had a restrictive impact on *Acidithiobacillus ferrooxidans.* Their capability of ferrous oxidizing would be completely suppressed when the Mo concentration in 9 K medium reached 2 mmol/L. Consequently, the dissolution of Mo via the oxidization by the bacterially generated Fe (III) is hindered.

In view of this, the solutions that can fulfill more efficient leaching of Mo include: 1) leaching bacteria with higher resistivity to the toxicity of Mo, and 2) controlling Mo concentration. In this work, the bioleaching of nickel-molybdenum sulfide ore by the *sulfolobus metallics* in a membrane bioreator system is studied. *Sulfolobus metallics* is a thermophilic bacterium that can defy the toxicity of Mo in leaching solution. It was reported in previous work that bioleaching with acidophilic themophile *Acidianus brierleyi* in many kinds of reactor such as batch and continuous-flow stirred tank reactor had been progressive [9−13]. Membrane bioreactor (MBR) is the combination of a membrane process with a bioreactor. It is generally applied in wastewater treatment to produce effluent water with the quality in line with the environmental regulation. In the present work, the membrane inside MBR is designed in such a way that it only allows the transport of Mo dissolved in the solution to the permeation side, so as to decrease the Mo concentration

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in the leaching solution.

2 Experimental

2.1 Materials

2.1.1 Mineral

The minerals in this study were the natural molybdenum ores obtained from a mine in Guizhou Province, China, with the main components being NiS_2, Ni_3S_4, NiAsS, NiS, Fe, MnS_4, and MoS_2. The nickel and molybdenum compounds are associated together to form a kind of glue called jordisite; therefore, MoS_2 can not be detected by XRD analysis. Mineralogy analysis showed that this jordisite contains not only sulfur (S) and Mo, but also carbon (C), hence is usually called Mo-C-S composite mineral. The naturally obtained mineral samples were dried, ground and then sieved to obtain particles with the size of 0.048−0.077 mm. The contents of major elements in the nickel-molybdenum ore are listed in Table 1.

2.1.2 Germ

The acidophilic thermophile used for leaching was *Sulfolobus metallicus* obtained from the Japan Collection of Microorganisms (Jcm). The original Jcm 8954 strain was adapted by multiple transfer technique to the leaching conditions [14]. Thereafter, the strain was subcultured aerobically at 65 °C for 7 d in the modified medium with pH value of 1.6(Their capabilities of ferrous oxidizing reached the maximum at this pH value) and was supplemented with 1% (w/v) nickel-molybdenum ore. The basal salts media 174 provided by Jcm are modified for the above cultivations. The modified media 174 are enriched with the following components (per liter of distilled water): $(NH_4)_2SO_4$ 130 mg; KH_2PO_4 280 mg; $MgSO_4 \cdot 7H_2O$ 250 mg; $CaCl_2 \cdot 2H_2O$ 70 mg; $FeCl_3 \cdot 6H_2O$ 20 mg; $MnCl_2 \cdot 4H_2O$ 1.8 mg; $Na_2B_4O_7 \cdot 10H_2O$ 4.5 mg; $ZnSO_4 \cdot 7H_2O$ 0.22 mg; $CuCl_2 \cdot 2H_2O$ 0.05 mg; $NaMoO_4 \cdot 2H_2O$ 0.03 mg; $VOSO_4 \cdot xH_2O$ 0.03 mg; $CoSO_4 \cdot 7H_2O$ 0.01 mg; yeast extract 1.0 g. The pH value was adjusted to 1.6 by using 6 mol/L H_2SO_4. The seven-day-old culture was removed from the modified medium and used in the subsequent experiment.

2.2 Apparatus

The picture of the bioleaching apparatus is shown in Fig. 1. The system comprises two different bioreactor systems. One system is the membrane bioreactor (MBR) with a membrane being installed for in-situ Mo removal; the other is a normal reactor without membrane. The membrane employed in the MBR is a kind of porous hollow fibres with pore size of around 0.5 μm (the ultrafiltration). It only allows the passage of ions of Mo, Ni and Fe in the leaching solution, whereas rejects the microbes. The controller board can adjust the leaching conditions including temperature and the distribution of mineral particles. The three plastic reactor cylinders (50 cm in height and 24 cm in diameter) were equipped with the aerators at the bottom for providing oxygen, with the controller of cycle for thermo regulator at both side round-bottomed plastic columns and with the membrane for filtration in the middle column.

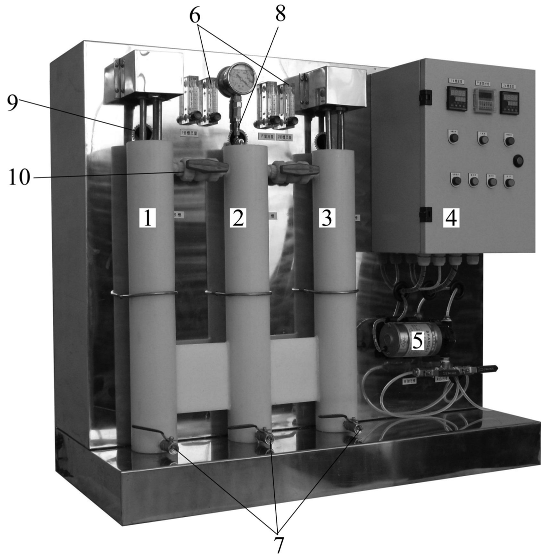

Fig. 1 Structure of MBR: 1, 2—Reactor column with membrane; 3—Reactor column without membrane; 4—Controller board; 5—Cycle pump; 6—Aeration; 7—Valve of collecting liquid or mineral residue; 8—Position for installing membrane; 9—Position for adding ores; 10—Valve for linking between reactor columns

Table 1 Composition of Ni-Mo ore (mass fraction, %)

O	Na	Mg	Al	Si	P	S	K	Ca	Ti
31.617	0.442	0.449	2.435	11.315	3.630	13.560	0.802	10.802	0.136
V	Mn	Fe	Co	Ni	Cu	Zn	Sr	Y	Zr
0.131	0.101	11.466	0.020	2.276	0.219	0.335	0.052	0.027	0.011
Mo	Pb	U	F	Cl	As	Se	Sb	Ba	Tl
4.353	0.113	0.128	0.363	0.050	1.501	0.195	0.042	0.663	0.115

The bioleaching in both MBR and the normal reactor was performed under the same conditions in terms of temperature, aeration and medium. A comparison between the two processes in the leaching rate of Ni and Mo can be made for evaluating the function of the membrane filtration on the leaching efficiency.

The other apparatus were F−2500 spectrometer, XSP−24N−103 bio-microscope, TZL16 centrifugal machine, THZ−82 vibration oscillator, and PE100 atomic absorber.

2.3 Bioleaching procedures

The bioleaching was performed according to the following procedures. Firstly, the two MBR columns and the normal column were loaded with the desired volume of modified media 174; then, the nickel-molybdenum ore samples were put into each column, respectively. Secondly, the seven-day-old adapted *Sulfolobus metallic* cells were inoculated into the leaching medium. Lastly, the controller of aeration, temperature and cycle device were turned on according to the set value. The initial cell density in the medium was 10% (v/v), while the nickel-molybdenum ore loading in leaching solution was around 100 g/L. The leaching liquid levels inside both the MBR and the column reactors were kept constant throughout the bioleaching process by supplementing the acid distilled water dropwise to make up for the evaporated water and by adding a certain quantity of the medium into MBR to replenish the filtered liquid. All the membrane filtering operation was carried out at a certain time interval and the volume of liquid to be treated in each filtering process depended on the concentration of Mo in leaching solution. In addition, the temperature and pH of MBR and its control were kept at 65 °C and 2 in the whole leaching periods.

3 Results and discussion

3.1 Optimization of aeration rate

Because oxygen is an important factor to the growth of microbe in leaching liquid, sufficient oxygen is necessary to bioleaching process. Previous researches showed that the oxygen solubility in the leaching liquid is determined by temperature and salinity of the leaching system. In the leaching system in the present work at 65 °C, the variation of oxygen concentration with aeration rate in the leaching liquid is displayed in Table 2. According to Ref. [15], the concentration range of dissolved oxygen for achieving the optimum performance in cell activity of *Sulfolobus metallicus* and the oxidizing effect of ferrous oxide is 2.50−4.25 mg/L. According to Table 2, the aeration rate was kept at 1.0 L/min in order to maintain the oxygen level in the leaching liquid.

Table 2 Relationship between oxygen concentration in leaching liquid and aeration rate

Aeration rate/($L\cdot min^{-1}$)	Oxygen concentration/($mg\cdot L^{-1}$)
0.5	3.17
1.0	3.23
1.5	3.22
2.0	3.23
2.5	3.25
3.0	3.21

The effect of aeration rate on the oxidizing of Fe^{2+} to Fe^{3+} by microorganism after 96 h of cultivation is summarized in Table 3. As can be seen, the highest rate of Fe^{2+} oxidization to Fe^{3+} is obtained with aeration rate of 1.0 L/min. Therefore, this aeration rate was selected for the subsequent bioleaching process.

Table 3 Relationship between aeration rate and microbiologically ferrous oxidizing at 65 °C after 96 h of cultivation

Aeration rate/($L\cdot min^{-1}$)	Fe^{2+}oxidized/%
0.5	68.11
1.0	79.23
1.5	78.65
2.0	77.34
2.5	78.55
3.0	76.56

The bioleaching in the MBR was carried out for 12 d under the chosen conditions. Table 4 shows that the higher leaching rates of Ni and Mo were obtained at the aeration rates of 1.0, 1.5 and 2.0 L/min, but the maximum leaching rates of Ni and Mo were reached when the aeration rate of 1.0 L/min was applied in this medium and special leaching environment. This result was consistent with the highest ability of the microorganism oxidizing Fe^{2+} under the same aeration condition.

Table 4 Impact of aeration rate on leaching rates of Ni and Mo

Aeration/($L\cdot min^{-1}$)	Ni leaching rate/%	Mo leaching rate/%
0.5	45.14	29.11
1.0	53.89	35.81
1.5	53.79	33.92
2.0	53.21	31.81

3.2 Leaching in column with and without microorganism

This experiment was performed at 65 °C, with the aeration rate of 1.0 L/min and mineral loading of 100 g/L in the solution. The Mo and Ni concentration variations in the process during 20 d leaching experiment are shown in Fig. 2 and Fig. 3, respectively. Finally, 75.24% Ni and 54.34% Mo in the column with microorganism were leached out; while only 45.89% Ni and 31.55% Mo were leached out in the control leaching process without microorganism.

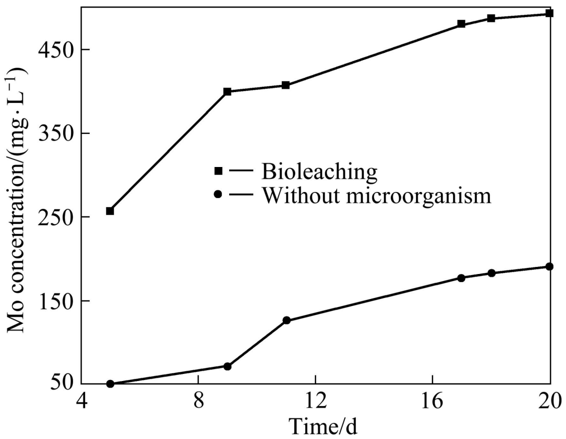

Fig. 2 Leaching rate of Mo with and without microorganism

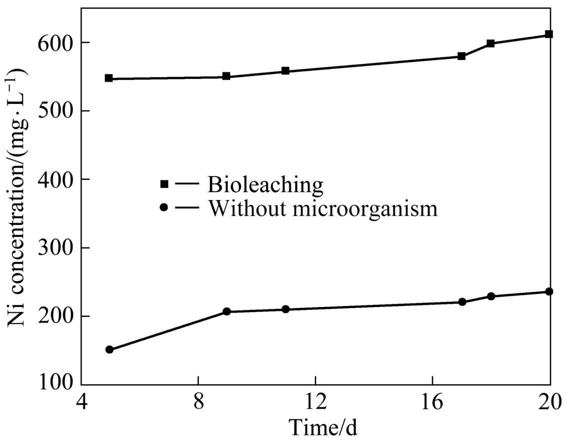

Fig. 3 Leaching rate of Ni with and without microorganism

3.3 Impact of Mo concentration in MBR leaching liquid on leaching rates of Ni and Mo

The MBR bioleaching was conducted in the two connected columns, with one column containing the membrane filtration system. The concentration of Mo in leaching liquid in MBR was maintained constant by the intermittent filtration using the microporous hollow fiber membranes. Different concentrations of Mo from 160 to 395 mg/L were applied. However, the concentration of Mo in the normal reactor without membrane was not controlled throughout the bioleaching process. The other experimental conditions were temperature 65 °C, aeration rate 1.0 L/min, mineral particle size 0.077 mm and pulp density 100 g/L for both the processes.

When the concentration of Mo in the MBR was maintained at 160 mg/L, the filtration of leaching solution was performed according to the concentration of Mo in leaching solution. The change of leaching rate with time in both the MBR and the control reactor is shown in Fig. 4. Obviously, the leaching rates of Ni and Mo in MBR were lower than those in the column without membrane. The final leaching rates of Ni and Mo in MBR after 20 d were 48.37% and 35.39%, respectively, while they were 75.66% and 53.98% in the column without membrane. Despite Mo was continuously removed to maintain its concentration lower than 160 mg/L, and its toxic inhibition to microorganism could be reduced, a substantial amount of Fe^{3+} was also taken away concurrently from the leaching liquid, resulting in the overall leaching rate decreasing. This experiment showed that the Mo concentration of 160 mg/L in the leaching liquid was too low to gain ideal leaching rates of Ni and Mo.

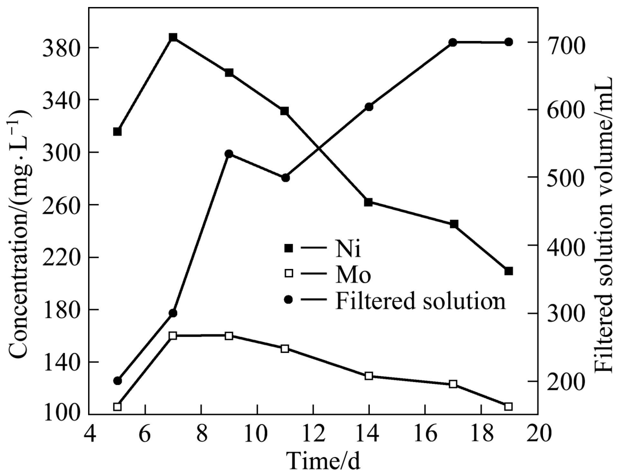

Fig. 4 Filtered solution volume and concentration of Ni and Mo in MBR leaching liquid under 160 mg/L of Mo

After bioleaching for 20 d under Mo concentration of 250 mg/L in leaching liquid and the other conditions above-mentioned, the leaching rates of Ni and Mo were 54.59% and 41.39% in the MBR, as shown in Fig. 5, respectively. But 74.98% Ni and 54.16% Mo were leached out from the column without membrane under the same conditions. From Fig. 5, it can be seen that the leaching rates of Ni and Mo were improved in the MBR, but still lower than those in the column without membrane that the microorganism was not restrained at the Mo concentration of 250 mg/L. After bioleaching for 20 d under 300 mg/L of Mo in leaching liquid and the other conditions above-mentioned, the leaching rates of Ni and Mo in the MBR were 66.19% and 46.33%, respectively, as shown in Fig. 6. But 74.98% Ni and 54.16% Mo were leached out form the column without membrane at the same condition. It is indicated that the leaching rates of Ni and Mo were still lower than those in the column without membrane at the same

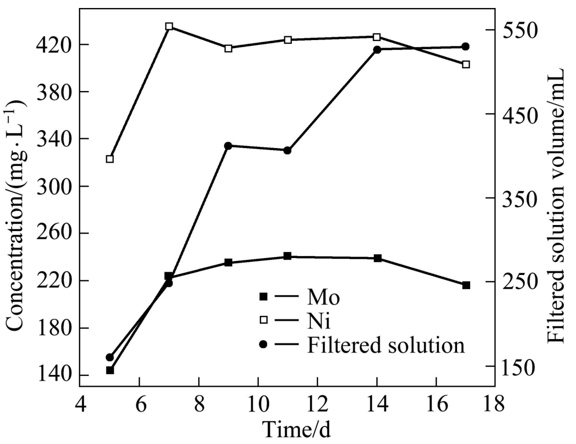

Fig. 5 Filtered solution volume and concentration of Ni and Mo in MBR leaching liquid under 250 mg/L of Mo

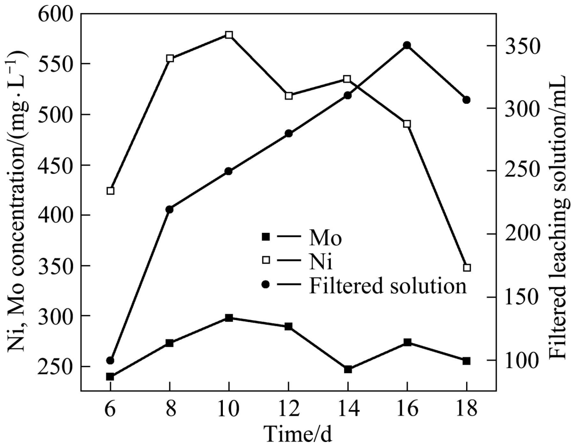

Fig. 6 Filtered solution volume and concentration of Ni and Mo in MBR leaching liquid under 300 mg/L of Mo

conditions. The possible reason is that excessive leaching liquid was filtered and the loss of Fe^{3+} into the permeated liquid has impact on the leaching action. After bioleaching for 20 d under 350 mg/L of Mo in leaching liquid and the other conditions above-mentioned, the leaching rates of Ni and Mo in the MBR were 70.79% and 49.98%, respectively. But 75.79% Ni and 54.33% Mo were leached out from the column without membrane under the same conditions. This result showed that although the leaching rates of Ni and Mo were improved remarkably, they are still lower than those in the column leaching without membrane. This experiment illustrated that the filtered liquid from leaching medium was still excessive and brought about the leaching results. After bioleaching for 20 d under 395 mg/L of Mo in leaching liquid and the other condition above-mentioned, the leaching rates of Ni and Mo in the MBR were 79.57% and 56.23%, respectively. But 75.26% Ni and 53.92% Mo were leached out from the column without membrance under the same conditions. The experiment results showed that the bioleaching in MBR at such a concentration of Mo leads to more leaching rates of Ni and Mo than in the column without membrane under the same condition. So a conclusion could be drawn that 395 mg/L of Mo is an optimum concentration when the nickel-molybdenum sulfide ore was bioleached with *Sulfolobus metallic* in the MBR. But this optimum concentration was not an unchangable value. It depended on the microorganism applied. This experiment results also showed that when the concentration of Mo in the leaching liquid exceeded 395 mg/L and *Sulfolobus metallic* was adopted, the membrane filter in MBR will play an important role in the leaching of nickel-molybdenum sulfide ore.

3.4 Components of nickel-molybdenum sulfide ore and its leaching residue

The components of nickel-molybdenum sulfide ore were detected by XRD analysis. As shown in Fig. 7, the ore mainly contains SiO_2, NiS_2, Fe_2SiO_4, $FeMoO_4$, $NiMoO_4$, $Ca_3(SiO_4)O$ and FeS_2. After leaching for 20 d, the components of the leaching residues are shown in Fig. 8. It can be seen that the components of residue are different from those of the ores. The main components include SiO_2(major), FeS_2(minor), $Al_2Si_2O_5(OH)_4$(minor), $MgAl_2O_4$, Fe_2O_3, $Ca(SiO_3)$(minor), $Fe_3(Si_{1.4}Fe_{0.6})$-$O_5(OH)_4$ (minor), Al_2O_3 (minor). SiO_2 is the most major compounds in the mineral and its residues.

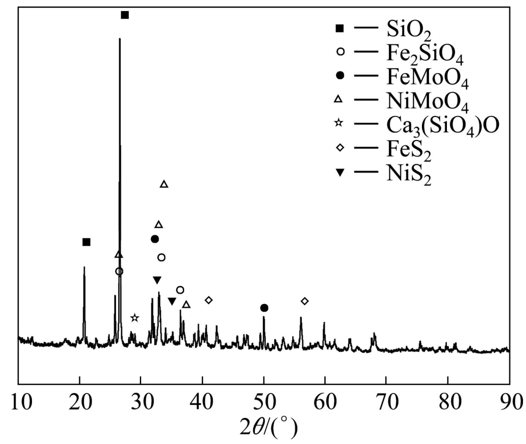

Fig. 7 XRD pattern of Ni-Mo ore

3.5 Ratio of Fe^{2+}/Fe^{3+} and total Fe ion concentration of bioleaching

The ratio of Fe^{2+}/Fe^{3+} and the total Fe ion concentration in the filtrate in the MBR and column system without membrane are shown in Fig. 9 and Table 5, respectively. It is revealed that the Fe^{2+}/Fe^{3+} ratio decreased with prolonging leaching time. Among them, the ratio of Fe^{2+}/Fe^{3+} at Mo 395 mg/L reached the minimum value. In other words, Fe^{3+} concentration increased remarkably with prolonging the leaching time when the concentration of Mo was kept at 395 mg/L

Table 5 Change of total Fe ion concentration in leaching process

Time/d	MBR leaching				Column leaching
	ρ(Mo)=160 mg/L	ρ(Mo)=250 mg/L	ρ(Mo)=350 mg/L	ρ(Mo)=395 mg/L	
9	400.89	454.13	502.69	582.14	589.38
11	473.98	513.43	564.67	654.46	595.29
14	463.59	497.46	579.91	683.16	619.47
17	421.57	498.05	590.35	599.28	616.76

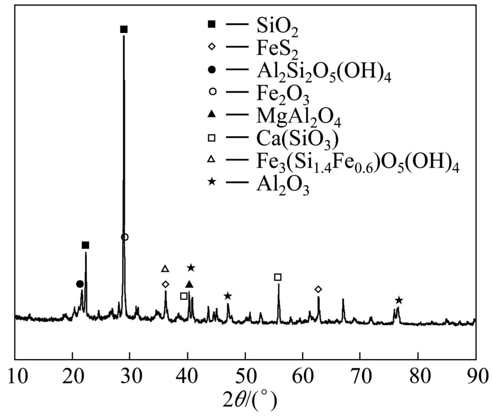

Fig. 8 XRD pattern of leaching residue

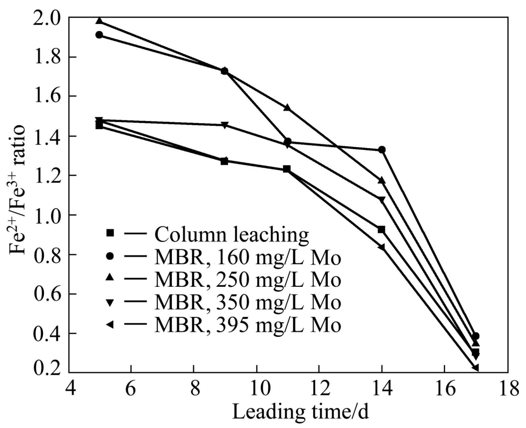

Fig. 9 Fe^{2+}/Fe^{3+} ratio in leaching of MBR and its control

in the leaching liquid. The total Fe ion concentration in leaching liquid increased with Mo concentration increasing from 160 mg/L to 395 mg/L, as shown in Table 5.

3.6 Change of cell number in process of bioleaching of MBR and column leaching

The change of cell number at different concentrations of Mo in MBR and column leaching is shown in Fig. 10. From Fig. 10, it can be found that the cell number increased rapidly in the first 7 d when the concentration of Mo was controlled at 160 mg/L. But they had almost the same increasing rate after 10 d and reached the maximum at 13 d or so for all tests, and kept unchanged till the end of leaching. But in the column leaching without membrane, it decreased gradually with prolonging leaching time.

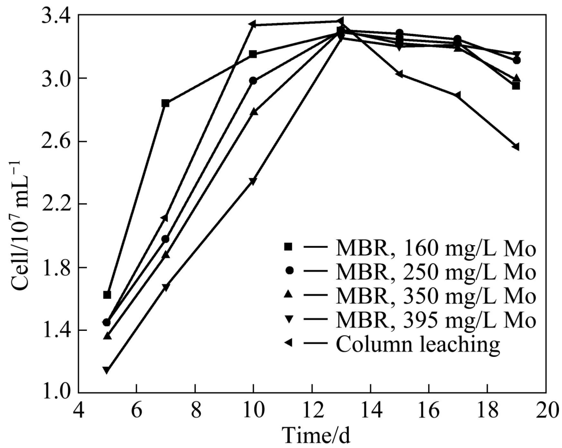

Fig. 10 Cell number change in MBR leaching and column leaching

4 Conclusions

1) The aeration has impact on the bioleaching rates of Ni and Mo. Leaching experiment in MBR showed that the optimum aeration rate was 1.0 L/min in MBR leaching.

2) When the concentration of Mo was kept at 395 mg/L in the MBR bioleaching process, the leaching rates of Ni and Mo reached the maximum values. This concentration of Mo in MBR avoided the toxicity of Mo to microbe and played the role of Fe^{3+} of oxidation to the mineral.

3) The leaching rate of Ni was higher than that of Mo. The reason was related to various factors including composition of mineral, crystal lattice, surface ion energy, potential, conductance and so on.

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膜生物反应器浸出镍钼矿

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摘　要：采用对钼有一定耐受性的嗜热金属硫叶菌结合膜反应器浸出镍钼矿。结果表明：由于膜生物反应器(MBR)中膜的过滤作用，使浸出液中的钼浓度保持在该菌可以耐受的范围内，从而实现细菌对矿物相对高效的浸出。在矿浆浓度 100 mg/L、通气量 1.0 L/min 下，将 MBR 浸出液中钼被控制在不同浓度，镍、钼的浸出率各不相同。当 MBR 浸出液中钼的浓度不超过 395 mg/L 时，镍和钼的浸出率达到 79.57%和 56.23%；而在相同条件下的柱浸，镍、钼浸出率为 75.59%和 54.33%，低于相同条件下 MBR 浸出。

关键词：膜生物反应器；镍钼矿；金属硫叶菌；生物浸出；钼毒性

(Edited by YUAN Sai-qian)