Determination of calcium and magnesium in bioleaching solution of uranium ore by optimized EDTA method

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Keywords: uranium ore, bioleaching solution, mixed indicator, calcium, magnesium

Abstract. This paper determined calcium and magnesium in bioleaching solution of uranium ore by optimized EDTA method. This method used acid chrome blue K-naphthol green B mixed indicator after adding reducing agent hydroxylamine hydrochloride, masking agent triethanolamine and masking agent L-cysteine. This method required the concentration of calcium and magnesium more than 0.50g/L, respectively. Thus, coexisting ions did not interfere with the determination, and the titration end point was obvious. The results show that the standard addition recovery rate of calcium and magnesium is 99.15%~101.40% and 99.26%~101.18%, respectively. The relative standard deviation of calcium and magnesium is less than 3.5% with good accuracy and precision. This method is simple and fast to determine calcium and magnesium in bioleaching solution of uranium ore, and the results are accurate and reliable.

Introduction

Bioleaching solution of uranium ore contains calcium, magnesium, potassium, sodium, iron, aluminum, lead, zinc, uranium, sulfate, phosphate, fluorine, chlorine and other ions. Currently, determination methods of calcium and magnesium in bioleaching solution of ore mainly contain EDTA titration [1-4], atomic absorption spectrometry and spectrophotometry. EDTA titration and atomic absorption spectrometry are commonly used to determine calcium and magnesium in bioleaching solution of ore.

GB/T 11848.15-1991 Determination of iron, calcium, magnesium, molybdenum, titanium and vanadium in uranium ore concentrate by atomic absorption spectrometry [5], uranium in processed sample solution needs to be separated from other elements by Levextrel chromatographic column. The effluent liquid from Levextrel chromatographic column is determined by atomic absorption spectrometry. GB/T 11848.14-1991 Determination of potassium and sodium in uranium ore concentrate by atomic absorption spectrometry [6], potassium and sodium are determined by atomic absorption spectrometry after uranium being adsorbed with ion exchange resin. Calcium and magnesium in bioleaching solution of uranium ore are determined by atomic absorption spectrometry after uranium being separated from other elements. The process is complex and it needs long time.

Calcium and magnesium in bioleaching solution of uranium ore are determined by EDTA method using calcium indicator and chrome black T after adding reducing agent hydroxylamine hydrochloride, masking agent triethanolamine and masking agent ethylenediamine. However, the titration end point is not obvious. Calcium and magnesium need to be separated from coexistence of interfering ions by ion exchange resin and then are determined by EDTA method. The process is

complex and it also needs long time. In addition, the chrome black T is blocked because of the masking agent triethanolamine.

Calcium and magnesium in bioleaching solution of uranium ore are determined by optimized EDTA method in this work. Mixed indicator is used after adding reducing agent and masking agent. Coexisting ions do not interfere with the determination, and the titration end point is obvious. The experimental results are with good accuracy and precision. This method is simple and fast to determine calcium and magnesium in bioleaching solution of uranium ore, and the results are accurate and reliable.

Experimental

Instruments and reagents: 50.00mL Acid burette; hydrochloric acid (ρ=1.19g/mL); nitric acid (ρ=1.42g/mL); sulfuric acid (ρ=1.84g/mL); hydroxylamine hydrochloride; triethanolamine (1+4); L-cysteine (10g/L); potassium hydroxide solution (200g/L); ammonia-ammonium chloride buffer solution (pH≈10); EDTA standard solution (f_{Ca}=0.9579mg/mL; f_{Mg}=0.5809mg/mL).

Acid chrome blue K-naphthol green B mixed indicator (K-B indicator): 0.5g Acid chrome blue K, 1.0g naphthol green B and 98.5g dry sodium chloride were weighed and then they were ground to a fine powder. The powder was stored in a brown bottle with a cover, and it could be used for a long time.

Experimental water is deionized water, and experimental reagents are analytical reagents.

Sample preparation: Parallel bioleaching solution of uranium ore was pipetted into the 250mL beaker, respectively. One was used to measure calcium, and the other was used to measure calcium and magnesium. Then 5.0mL nitric acid and 2.0mL sulfuric acid were added to the beaker. The hot plate was switched on and the beaker was heated until white smoke of sulfur trioxide was over. After that, the beaker was removed and placed to room temperature. Then 1.0~2.0mL hydrochloric acid and 20.0mL distilled water were added to the beaker, and it was placed on the hot plate to boil until the salts were completely dissolved. Finally, the beaker was removed and placed to room temperature. The solution in the beaker was prepared to be titrated (be-titrated solution).

Sample analysis: Be-titrated solution was made to 50.0mL with water and then was shaken up.

Calcium: 0.2~0.3g Hydroxylamine hydrochloride, 5.0mL triethanolamine (1+4) and 5.0mL L-cysteine (10g/L) were added to one be-titrated solution and then was shaken up. After that, 10.0mL potassium hydroxide solution (200g/L) and 0.1~0.2g K-B indicator were added to the be-titrated solution and then was shaken up. The pH of the be-titrated solution was 12 and the color of it was wine red. The be-titrated solution was titrated with EDTA until the wine red disappeared and blue appeared. Concentration of calcium ion could be calculated.

Calcium and magnesium: 0.2~0.3g Hydroxylamine hydrochloride, 5.0mL triethanolamine (1+4) and 5.0mL L-cysteine (10g/L) were added to the other be-titrated solution and then was shaken up. After that, 10.0mL ammonia-ammonium chloride buffer solution (pH≈10) and 0.1~0.2g K-B indicator were added to the be-titrated solution and then was shaken up. The pH of the be-titrated solution was 10 and the color of it was wine red. The be-titrated solution was titrated with EDTA until the wine red disappeared and pure blue appeared. Concentration of magnesium ion could be calculated.

Results and Discussion

Amount of masking agent experiments: Be-titrated solution was made to 50.0mL with water and then was shaken up. 0.2~0.3g Hydroxylamine hydrochloride was added to the be-titrated solution

and then was shaken up. 1.0, 3.0, 5.0, 7.0, 10.0, 12.0, 15.0mL Triethanolamine (1+4) and 1.0, 3.0, 5.0, 7.0, 10.0, 12.0, 15.0mL L-cysteine (10g/L) were added to the be-titrated solution. Other steps were completed in accordance with sample analysis. The experimental results are shown in Table 1.

Table 1 Amount of masking agent experiments

Volume of triethanolamine [mL]	1.0	3.0	5.0	7.0	10.0	12.0	15.0
Volume of L-cysteine [mL]	1.0	3.0	5.0	7.0	10.0	12.0	15.0
Concentration of calcium ion [$g.L^{-1}$]	0.53	0.53	0.52	0.52	0.53	0.53	0.53
Concentration of magnesium ion [$g.L^{-1}$]	1.21	1.20	1.17	1.17	1.18	1.21	1.22

Table 1 shows that the results are basically unchanged when the amount of masking agent triethanolamine and L-cysteine is between 1.0~12.0mL. The masking of iron ion and aluminum ion is not complete when the amount of masking agent triethanolamine and L-cysteine is 1.0mL, and so the results are higher than accurate results. K-B indicator is blocked when the amount of masking agent triethanolamine and L-cysteine is 12.0mL, and so the results are also higher than accurate results. 5.0mL Triethanolamine and 5.0mL L-cysteine are selected from the point of experimental cost and operation convenience.

K-B indicator proportion experiments: Be-titrated solution was made to 50.0mL with water and then was shaken up. 0.2~0.3g Hydroxylamine hydrochloride, 5.0mL triethanolamine (1+4) and 5.0mL L-cysteine (10g/L) were added to the be-titrated solution and then was shaken up. After that, 10.0mL potassium hydroxide solution (200g/L) or 10.0mL ammonia-ammonium chloride buffer solution (pH≈10) and 0.1~0.2g K-B indicator were added to the be-titrated solution and then was shaken up. Other steps were completed in accordance with sample analysis. The experimental results are shown in Table 2.

Table 2 K-B indicator proportion experiments

Mass of acid chrome blue K [g]	1.0	0.5	1.0	0.5	1.0
Mass of naphthol green B [g]	0.5	0.5	1.5	1.0	2.5
Titration end point of calcium	N	N	N	Y	N
Titration end point of calcium and magnesium	N	N	Y	Y	Y

Table 2 shows that the titration end point of calcium is from wine red to blue when K:B is 1:2. The titration end point of calcium and magnesium is from wine red to pure blue when K:B is 1:1.5, 1:2, 1:2.5. K:B=1:2 is selected in order to use the same proportion like the determination of calcium.

Recovery experiments: Table 3 shows that the standard addition recovery rate of calcium is 99.15%-101.40%. Table 4 shows that the standard addition recovery rate of magnesium is 99.26%-101.18%. This method has good accuracy.

Table 3 Recovery experiments of calcium

Number	Concentration [$g.L^{-1}$]	Amount [mg]	Recovery [mg]	Recovery [%]
1#	0.52	5.0	4.972	99.44
	0.52	10.0	10.126	101.26
2#	0.60	5.0	4.9575	99.15
	0.60	10.0	10.140	101.40

Table 4 Recovery experiments of magnesium

Number	Concentration [g.L^{-1}]	Amount [mg]	Recovery [mg]	Recovery [%]
1#	1.17	10.0	10.118	101.18
	1.17	20.0	19.852	99.26
2#	1.06	10.0	9.957	99.57
	1.06	20.0	19.974	99.87

Precision experiments: Table 5 shows that the relative standard deviation of calcium and magnesium is 2.4%~3.3% and 1.1%~2.8%, respectively. This method has good precision.

Table 5 Precision experiments

Number	Element	Results of experimental method [g.L^{-1}]						Average [g.L^{-1}]	RSD [%]
1#	Ca	0.53	0.52	0.54	0.53	0.51	0.51	0.52	2.4
	Mg	1.17	1.16	1.16	1.18	1.19	1.16	1.17	1.1
2#	Ca	0.61	0.60	0.59	0.63	0.59	0.58	0.60	3.0
	Mg	1.11	1.05	1.06	1.08	1.03	1.04	1.06	2.8
3#	Ca	0.54	0.52	0.51	0.56	0.54	0.53	0.53	3.3
	Mg	1.11	1.16	1.14	1.12	1.11	1.17	1.14	2.3

Conclusions

Calcium and magnesium in bioleaching solution of uranium ore are determined by optimized EDTA method under the condition of 5.0mL triethanolamine, 5.0mL L-cysteine and K:B=1:2. The standard addition recovery rate of calcium and magnesium is 99.15%~101.40% and 99.26%~101.18%, respectively. The relative standard deviation of calcium and magnesium is less than 3.5% with good accuracy and precision.

Acknowledgements

The authors gratefully acknowledge Professor Song Yongsheng and the financial support of National Natural Science Foundation of China (NO. 51404031).

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