

## Extraction of cobalt from laterite ores by citric acid in presence of ammonium bifluoride

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**Abstract:** Citric acid was used to selectively extract cobalt from limonite-type laterite ores in the presence of ammonium bifluoride. The results show that ammonium bifluoride enhances the leaching of cobalt by citric acid, and 84.5% cobalt is extracted from a laterite ore containing 0.13% Co when leached at ambient temperature for 2 h with 30 g/L citric acid and 10 g/L ammonium bifluoride. Pyrolusite is reduced by citric acid during leaching, cobalt intergrown with which is liberated and subsequently chelated by the citric acid. The extraction of cobalt is enhanced in the presence of ammonium bifluoride because the matrix of silicate minerals is destroyed by ammonium bifluoride and the adsorbed cobalt is subsequently liberated.

**Key words:** laterite; cobalt; citric acid; ammonium bifluoride

## 1 Introduction

Cobalt is an important strategic metal, which is extensively utilized in modern industry. The vast majority of cobalt resources are preserved in laterite ores which are becoming the predominant sources of cobalt[1]. Exploitation of laterite ores is becoming increasingly important with the increasing demand for cobalt all over the world[2].

Conventional methods, including pyrometallurgical and hydrometallurgical processes, were usually focused on the utilization of nickel in laterite ore, and more attention was paid to the recovery of nickel than that of cobalt. In fact, cobalt recovery provided an important revenue contribution to these processing projects[3]. Otherwise, it was evident that pyrometallurgical processes were characterized by a low recovery of cobalt in practice, was the reduction roasting-ammonia leaching process. High-pressure acid leaching (HPAL) process presented both costing and operating issues although cobalt recovery is as high as 90%[4]. Biometallurgical techniques possess many merits such as little environmental pollution and low cost.

Extraction of metals from laterite ores by the

organic acid metabolites produced by microbe had been reported recently[5]. Several technical problems such as too long leaching time and low metal recovery must be resolved before its industrial application, but high selectivity for leaching metals by organic acid implies an effective method to selectively extract specific metals from laterite ores. Citric acid was proved to be the most effective organic acid to extract nickel from serpentine-type laterite ores, but inefficient to leach nickel from limonite-type laterite ores due to its low reactivity with goethite, in which nickel was involved[6–7].

In this work, extraction of cobalt from limonite-type laterite ores was studied by citric acid, and ammonium bifluoride was used to enhance the leaching process.

## 2 Experimental

### 2.1 Materials

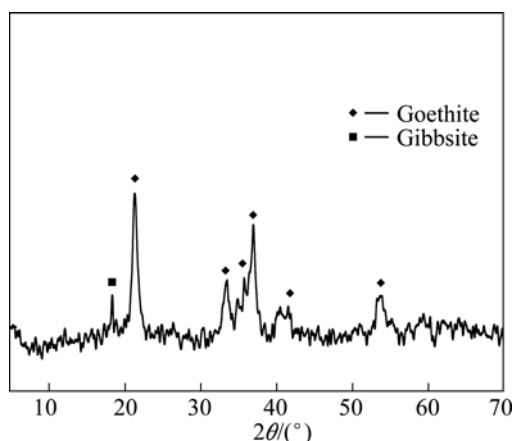
Both citric acid and ammonium bifluoride were analytically pure reagents.

Laterite ore sample was taken from Indonesia, which was characterized by a high content of cobalt, but relatively low content of nickel (see Table 1). X-ray diffraction analysis (Fig.1) indicated that the sample mainly contained goethite (FeOOH) and gibbsite

( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ); minority pyrolusite and poor-crystallized kaolinite were also found by optical microscopy. Surface scanning images obtained by SEM showed that nickel was mainly associated in goethite, while cobalt was mainly intergrown with manganese and silicate minerals.

**Table 1** Main chemical compositions of laterite (mass fraction, %)

Co	Ni	MgO	$\text{Al}_2\text{O}_3$	$\text{MnO}_2$	$\text{SiO}_2$	Total iron grade
0.13	1.03	0.98	9.72	1.25	4.25	43.95



**Fig.1** XRD pattern of laterite ore sample

## 2.2 Methods

Leaching tests were conducted in a DY-8 autoclave, which was designed and made in Central South University, China. The autoclave was equipped with eight 150 mL stainless steel bombs which could rotate end to end (the rotating velocity ranging from 20 to 120 r/min) in a bath of glycerine. The glycerine bath was electrically heated, and leaching temperature was controlled by thermostat. At the beginning of each trial, laterite ground to 90% undersize 74  $\mu\text{m}$  was added into the bombs and mixed with citric acid, ammonium bifluoride liquor, and the leaching liquid-to-solid ratio was fixed at 10. Thereafter, the sealed bombs were soaked in the bath at given temperature and agitated at 23 r/min. Filtration was performed immediately after leaching for a given period, and the leached residue was dried and sampled for cobalt content analysis. Subsequently, the leaching rate of cobalt was calculated as follows:

$$\gamma = (1 - \frac{m_0\beta}{m_1\alpha}) \times 100\% \quad (1)$$

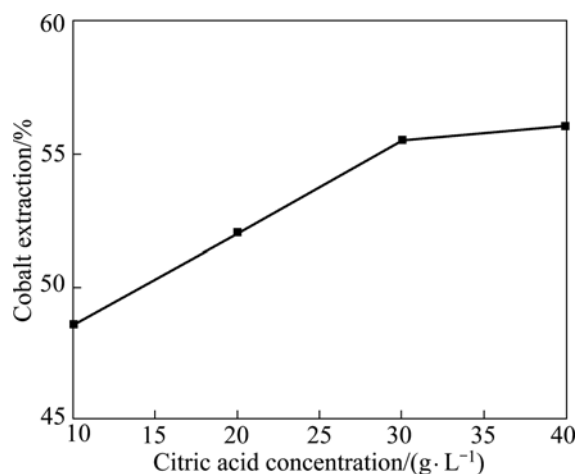
where  $\gamma$  is the leaching rate of cobalt, %;  $m_1$  is the mass of sample before leaching, g;  $\alpha$  is the cobalt content of raw material, %;  $m_0$  is the mass of leached residue, g;  $\beta$  is the cobalt content of leached residue, %.

## 3 Results and discussion

### 3.1 Leaching experiments

#### 3.1.1 Effects of citric acid concentration

The extraction of cobalt as a function of citric acid concentration is given in Fig.2. The samples were leached at 70 °C for 4 h. It can be seen that the extraction of cobalt increases with increasing the citric acid concentration; however, the cobalt extraction is imperfect; the maximum extraction of cobalt is as low as 55.4%. Therefore, it is necessary to enhance the cobalt extraction with citric acid.



**Fig.2** Effects of citric acid concentration on extraction of cobalt

#### 3.1.2 Effects of ammonium bifluoride concentration

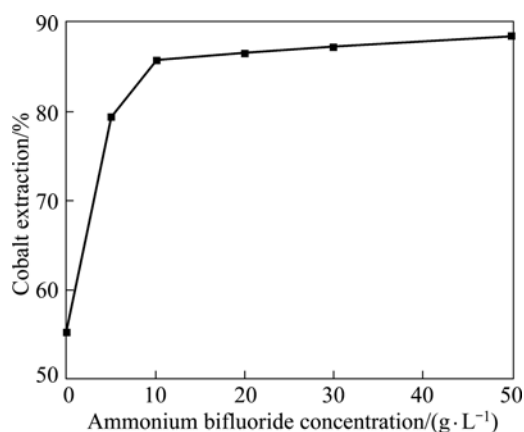
Process mineralogy showed that a portion of cobalt was associated with clay mineral, resulting in low cobalt extraction by citric acid. Hydrofluoric acid was usually used to dissolve clay minerals because it destroyed Si—O, Al—O and Al—O—Si bonds and formed stable Si—F bonds. However, hydrofluoric acid was highly corrosive, toxic and hazardous, so ammonium bifluoride was used in practice[8–11].

The effects of ammonium bifluoride on the cobalt extraction are shown in Fig.3. For these tests, the samples were leached at 70 °C for 4 h, and citric acid concentration was 30 g/L.

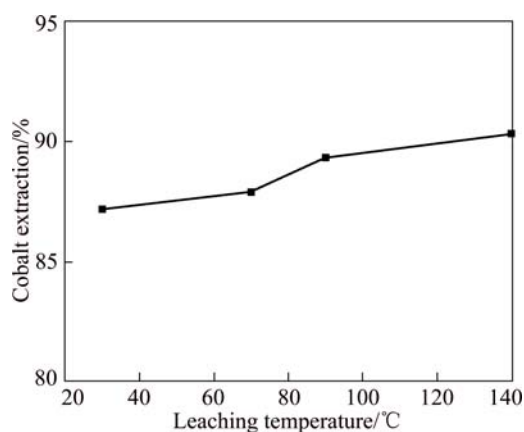
Ammonium bifluoride is capable of improving cobalt extraction, and the extraction of cobalt is increased from 55.4% to 85.7% with the addition of 10 g/L ammonium bifluoride. However, only a little increase of cobalt extraction is achieved when ammonium bifluoride concentration is increased further.

#### 3.1.3 Effects of leaching temperature

The effects of leaching temperature on the extraction of cobalt were conducted under the conditions of 30 g/L citric acid, 10 g/L ammonium bifluoride, and 4 h leaching time. In Fig.4, the higher the temperature is,



**Fig.3** Effects of ammonium bifluoride concentration on extraction of cobalt

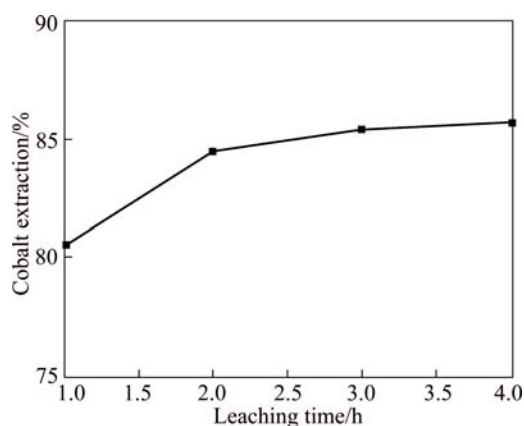


**Fig.4** Effects of leaching temperature on extraction of cobalt

the more the cobalt is leached; cobalt extraction is increased from 84.5% to 92.0% with increasing temperatures from 30 °C to 140 °C. Generally, it is more practical to leach at ambient temperature, because of lower energy consumption.

#### 3.1.4 Effects of leaching time

The extraction of cobalt is given in Fig.5 as a



**Fig.5** Effects of leaching time on extraction of cobalt

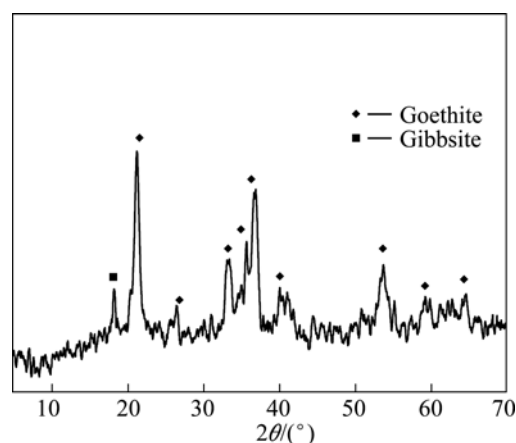
function of leaching time at 30 °C by using 30 g/L citric acid and 10 g/L ammonium bifluoride. The results show that the effect of leaching time on the extraction of cobalt is almost imperceptible when it exceeds 2 h.

It can be concluded from the above results that the suitable leaching conditions are citric acid concentration of 30 g/L, ammonium bifluoride of 10 g/L and leaching at ambient temperature for 2 h. And 84.5% cobalt is leached under these conditions.

### 3.2 Leaching mechanism by citric acid and ammonium bifluoride

Fig.6 shows that the main mineral constituents of leached residue are similar to the raw ore (see Fig.1), which indicates that goethite and gibbsite are not dissolved significantly by citric acid and ammonium bifluoride.

The main chemical compositions of leached residue are listed in Table 2.



**Fig.6** XRD pattern of leached residue

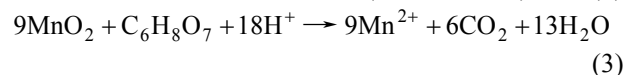
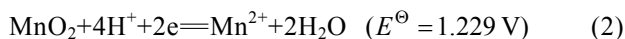
**Table 2** Main chemical compositions of leached residue (mass fraction, %)

Co	Ni	MgO	Al <sub>2</sub> O <sub>3</sub>	MnO <sub>2</sub>	SiO <sub>2</sub>	Total iron grade
0.025	0.87	0.76	9.36	0.48	2.23	43.18

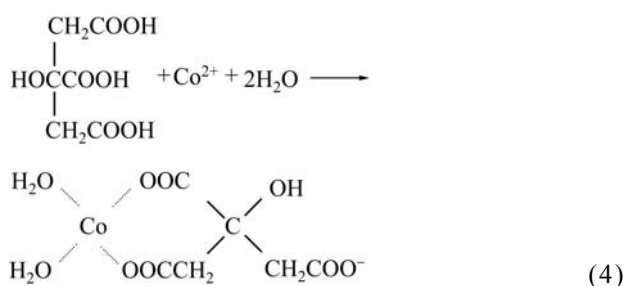
From a comparison between Tables 1 and 2, it can be found that the cobalt, MnO<sub>2</sub> and SiO<sub>2</sub> contents of the leached residue are much lower than those of the raw ore, which indicates effective leaching of these elements by citric acid and ammonium bifluoride. However, small decreases of nickel, MgO, Al<sub>2</sub>O<sub>3</sub> contents and total iron grade show that small amounts of them are dissolved into liquor. The results confirm the selective extraction of cobalt over nickel and iron.

Citric acid is an organic reductant, which is able to reduce some high valence metal ions. The reduction of Cr<sup>6+</sup> to Cr<sup>3+</sup> by citric acid was reported in Ref.[8].

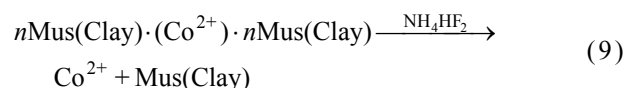
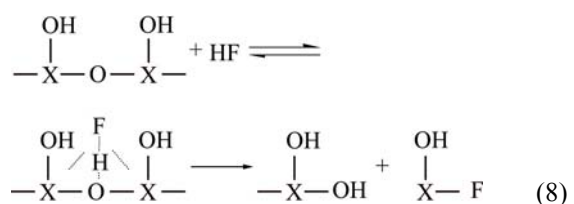
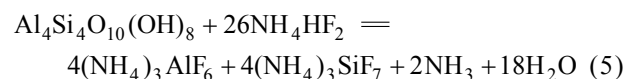
Pyrolusite is an oxidizer in acidic liquor, whose standard electric potential is as high as 1.229 V (Eq.(2)). Therefore, pyrolusite was reduced by citric acid and dissolved into liquor as  $\text{Mn}^{2+}$ , and the associated cobalt was liberated simultaneously (Eq.(3))[9–10]:



whereafter, the liberated cobalt further reacted with citric acid to form soluble metal chelates, and the reaction was expressed as (Eq.(4))[11]:



Nevertheless, the cobalt associated in clay minerals is inefficient to be leached solely by citric acid. Clay minerals such as kaolinite are destroyed by ammonium bifluoride (Eqs.(4)–(6)). Dissolution of silicate minerals is wholly attributed to  $\text{HF}$  molecules rather than  $\text{F}^-$  in the solution. The model of silicate dissolution by  $\text{HF}$  was presented in (Eq.(7))[12–14]. Therefore, cobalt was liberated from the matrix of clay minerals, and then chelated by citric acid. The reaction of liberating  $\text{Co}^{2+}$  from clay minerals was expressed as (Eq.(8))[15]:



where X represents the lattice atom such as silicon or aluminum of silicates.

## 4 Conclusions

1) Cobalt in limonite-type laterite is able to be extracted by citric acid with aid of ammonium bifluoride.

An extraction of 84.5% cobalt is achieved when being leached at ambient temperature for 2 h by using 30 g/L citric acid and 10 g/L ammonium bifluoride, more than 29.1% Co is extracted when leaching by 30 g/L citric acid only.

2) Silicate minerals are dissolved by ammonium bifluoride, and cobalt associated with silicates is liberated and subsequently leached by citric acid. Therefore, the extraction of cobalt is obviously increased when leaching in the presence of ammonium bifluoride.

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