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Recovery of Valuable Metals with Citric Acid from Red Mud

Xiaobo Zhu, Wang Li, Sen Tang, Wenzhong Li
College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo Henan, 454000, China

ABSTRACT
The research has focused on the recovery of valuable metals with citric acid to strengthen leaching from red mud, which is obtained from bauxite during alumina production. The main factors on the recovery of valuable metals such as sulfuric acid concentration, liquid to solid ratio, citric acid addition, leaching temperature and leaching time were investigated. The XRD pattern of red mud and leached sample were analyzed. The results show that the main phases in red mud were perovskite, brookite, muscovite, hematite, calcite, cancrinite and quartz. The recovery of titanium, vanadium, iron and aluminum reached 81.36%, 66.72%, 78.42% and 71.64% respectively under the conditions of citric acid of 5%, sulfuric acid concentration of 5 mol/L, liquid to solid ratio of 5 mL/g, temperature of 90 ^{o}C and time of 60 min. The dissolution of perovskite, brookite, hematite, cancrinite and muscovite led to the recovery of titanium, vanadium, iron and aluminum, which could be promoted with using citric acid.
Keywords: Red mud; Valuable metals; Citric acid; Titanium; Vanadium.

I. INTRODUCTION

Red mud, the tailings during alumina production from bauxite, is a kind of alkaline solid waste (Xu and Luo, 1994; Li, 2007; Jiang et al., 2003). 1.0-1.6 tons of red mud is generated per ton of alumina and it is estimated that over 70 million tons of the waste are impounded annually in the world (Agatzini-Leonardou et al., 2008; Luo et al., 2002; Yang et al., 1999). Meanwhile, the rising tendency of red mud output is increasing year by year. The disposal of damming up process on red mud is expensive and causes environmental problems (Lai et al., 2008; Zhu and Qi, 2009).

Red mud is also a kind of complex mineral material, in which chemical and mineralogical compositions are varied depending upon the source of bauxite and the technological process parameters. It usually contains six major constituents, namely, $A1_2O_3$, Fe_2O_3, TiO_2, Na_2O, CaO and SiO_2 (Liu et al, 2012; Cao et al., 2013). Furthermore, small quantities of trace elements are also existed in red mud such as V, Sc, Ni, etc (Chai et al., 2001; Zhu and Lan, 2008; Indrani et al., 2011; Ochsenkühn and Lyberopulu, 1996; Smirnov and Molchanova, 1997).

Red mud could be applied in building materials, absorbents, fillers and catalysts. However, the recovery of valuable metals such as titanium and vanadium from red mud can not only realize resource recycling, but also contribute to reduce the pollution of environment and improve the comprehensive utilization of mineral resources (Nan et al., 2010). The extraction of valuable metals from Bayer process red mud was investigated with concentrated sulfuric acid (Cengloglu et al., 2001; Tsakiridis et al., 2011). The sulfuric acid concentration of 7 mol/L even 9 mol/L was needed for high recovery of titanium. Furthermore, a lot of acid leaching solution was obtained due to the high liquid to solid ratio during acid leaching (Zhu et al., 2011; Song et al., 2012; Wang and Li, 2012).

The present research work is to investigate the recovery of valuable metals with citric acid to strengthen leaching from red mud. The aim is to decrease sulfuric acid consumption and discuss the reaction mechanism of citric acid during acid leaching process.

II.EXPERIMENTAL

2.1. Materials

The red mud sample was collected from Henan province, China. The sample was very fine and did not need to crush for acid leaching. The sample was assayed by using inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the result is given in Table 1.

Table 1 The main chemical composition of red mud (wt. %)

Element	TiO_2	V_2O_5	Fe_2O_3	Al_2O_3	SiO_2	CaO	Na_2O	MgO	Sc_2O_3
Content	5.64	0.24	14.63	22.31	18.92	8.46	10.72	2.04	0.016

It was shown that the main compositions of this red mud were many metallic oxide such aluminum, ferrum, calcium, titanium and vanadium oxide, etc. The XRD pattern of the red mud sample is depicted in Fig. 1.

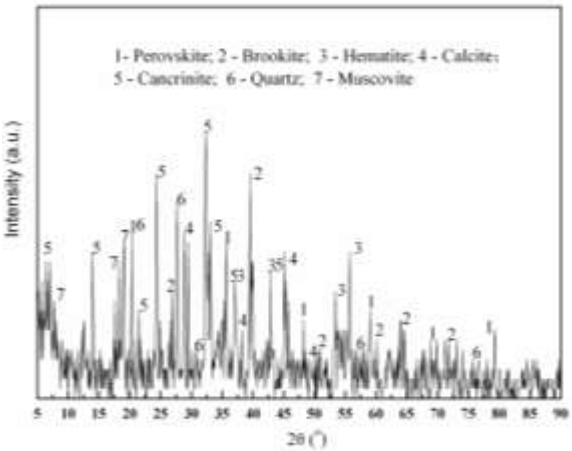

Fig. 1. The XRD pattern of the red mud sample.

It indicated that the main minerals in the red mud were perovskite, brookite, hematite, calcite, cancrinite, quartz and muscovite. Furthermore, it was found that titanium existed in perovskite and brookite, whereas vanadium mainly existed in muscovite in the form of lattice replacement by using electronic probe micro-analyzer.

The analytical purity chemical reagent including citric acid and sulfuric acid from Dengke Chemical Reagent Technology Co., Ltdwas used. The water used in this study was distilled water.

2.2. Methods

The red mud sample was first dried in a TE-DO130 drying oven (China) at 85 ^oC for 8 h, which was taken out of the drying oven and then cooled further to room temperature outside the drying oven. Then 20 g dried sample was adding some citric acid and mixing with the sulfuric acid solution of different concentration. Then, the ore slurry was stirred at the speed of 300 rpm under different conditions of time, temperature and liquid to solid ratio by using a KX79-1 magnetic heating mixer (China). The acid leaching solution was collected through filtration with a SHB-IIIA vacuum suction filter (China). The solid residue was dissolved in hydrofluoric acid solution, and then the content of valuable metals was determined by ICP-AES.

III. RESULTS AND DISCUSSIONS

3.1. Effect of sulfuric acid concentration

The effects of sulfuric acid concentration on recovery of valuable metals without and with adding 5% citric acid are illustrated in Fig. 2 and Fig. 3, respectively under the condition of liquid to solid ratio of 5 mL/g, temperature of 90 ^oC and reaction time of 60 min.

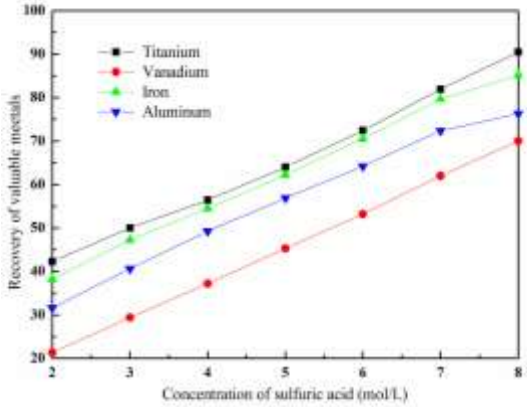

Fig. 2. Effect of sulfuric acid concentration on recovery of valuable metals.

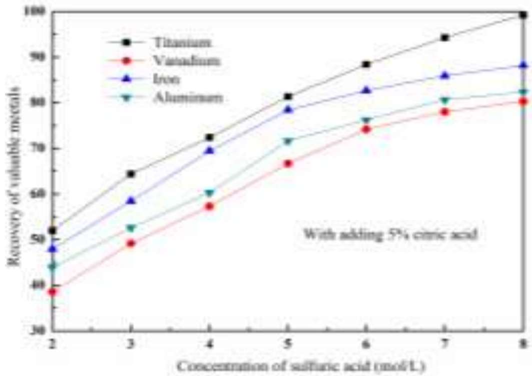

Fig. 3. Effect of sulfuric acid concentration on recovery of valuable metals with adding 5% citric acid.

It can be seen from Fig. 2 and Fig. 3 that the recovery of titanium can reach 80% using 7 mol/L sulfuric acid, but only 5 mol/L sulfuric acid was needed as the near titanium recovery was achieved with adding 5% citric acid. Therefore, the consumption of sulfuric acid has reduced by 30% with adding 5% citric acid. The increase tendency on recovery of vanadium, iron and aluminum was similar to titanium extraction with or without adding 5% citric acid. Overall, the recovery of titanium and iron was higher than that of aluminum and vanadium. The recovery of titanium, vanadium, iron and aluminum was 81.36%, 66.72%, 78.42% and 71.64%, respectively under the condition of sulfuric acid of 5 mol/L, citric acid of 5%, liquid to solid ratio of 5 mL/g, temperature of 90 ^oC and reaction time of 60 min.

3.2. Effect of liquid to solid ratio

The effects of liquid to solid ratio on recovery of valuable metals without and with adding 5% citric acid are illustrated in Fig. 4 and Fig. 5, respectively under the condition of sulfuric acid concentration of 5 mol/L, temperature of 90 ^oC

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and reaction time of 60 min.

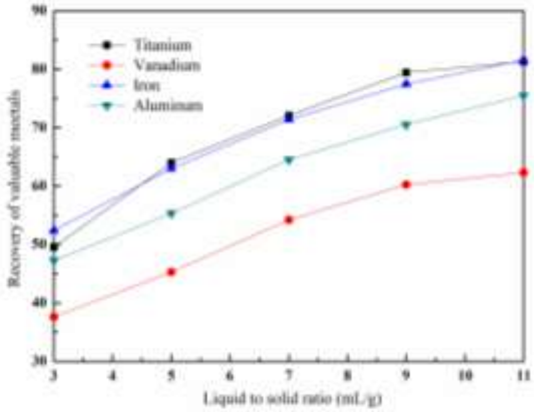

Fig. 4. Effect of liquid to solid ratio on recovery of valuable metals.

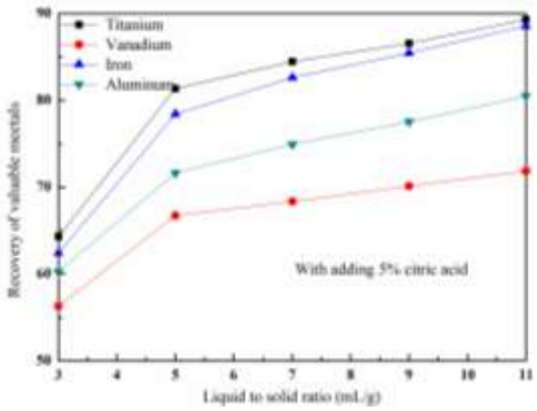

Fig. 5. Effect of liquid to solid ratio on recovery of valuable metals with adding 5% citric acid.

Fig. 4 and Fig. 5 show that the recovery of titanium, vanadium, iron and aluminum increased with increasing the liquid to solid ratio. The recovery of titanium, vanadium, iron and aluminum could reach 79.42%, 60.26%, 77.46% and 70.54% at liquid to solid ratio of 9 mL/g. Those were 81.96%, 66.72%, 78.42% and 71.64% at liquid to solid ratio of 5 mL/g with adding 5% citric acid. The increase of titanium, vanadium, iron and aluminum extractions was balanced as liquid to solid ratio without adding citric acid, whereas the increase was sharp in low liquid to solid ratio range, and became mild in the high liquid to solid ratio range with adding 5% citric acid. Therefore, the citric acid could not only decrease the sulfuric acid concentration, but also reduce the liquid to solid ratio in the acid leaching process.

3.3. Effect of citric acid addition

The effect of citric acid addition on recovery of valuable metals is shown in Fig. 6 under the condition of sulfuric acid concentration of 5 mol/L, liquid to solid ratio of 5 mL/g, temperature of 90 °C and reaction time of 60 min.

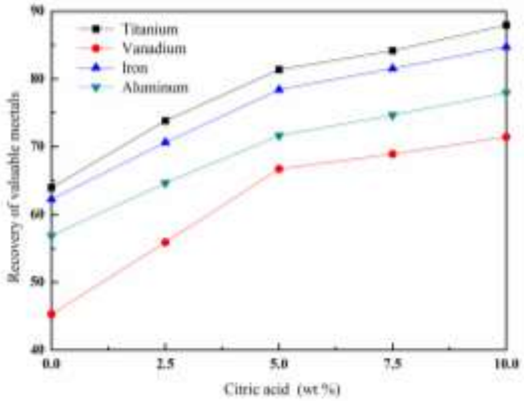

Fig. 6. Effect of citric acid on recovery of valuable metals.

It can be observed that the recovery of titanium, vanadium, iron and aluminum increased with increasing the citric acid addition. The increase was sharp in low citric acid addition range, and became mild in citric acid addition ratio range. The recovery of titanium, vanadium, iron and aluminum was 81.96%, 66.72%,78.42% and 71.64%, respectively with liquid to solid ratio of 5 mL/g at 5 mol/L sulfuric acid with adding 5% citric acid. Those were 86.31%, 71.43%, 83.74% and 77.97% with adding 10% citric acid. In addition, it was easier to filter for the leaching pulp of red mud with adding citric acid.

3.4. Effect of leaching temperature

The effect of leaching temperature on recovery of valuable metals is given in Fig. 7 under the condition of sulfuric acid concentration of 5 mol/L, citric acid of 5%, liquid to solid ratio of 5 mL/g and reaction time of 60 min.

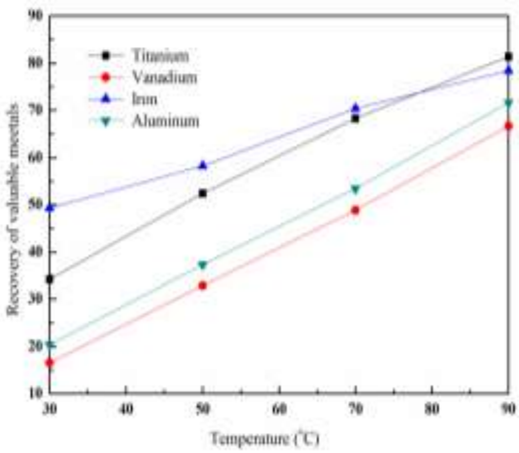

Fig. 7. Effect of leching temperature on recovery of valuable metals.

It can be observed that the recovery of titanium, vanadium, iron and aluminum increased sharply with increasing temperature from 30 to 90 ^oC. The recovery of titanium, vanadium, iron and aluminum was 35.46%, 16.21%, 49.36% and 20.34% respectively at 30 ^oC, whereas the values were 86.31%, 71.43%, 83.74% and 77.97% at 90 ^oC from Fig 7. In addition, the increase was still sharp at high temperature. Therefore the leaching temperature could increase in some conditions for higher recovery of valuable metals.

3.5. Effect of leaching time

The effect of leaching time on recovery of valuable metals is presented in Fig. 8 under the condition of sulfuric acid concentration of 5 mol/L, citric acid of 5%, liquid to solid ratio of 5 mL/g and temperature of 90 ^oC.

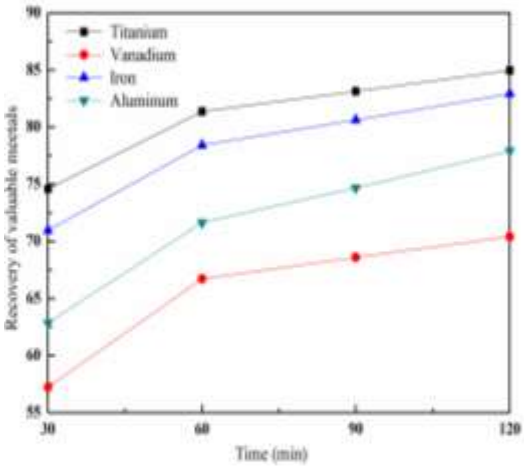

Fig. 8. Effect of leaching time on recovery of valuable metals.

It can be seen that the recovery of titanium, vanadium, iron and aluminum increased sharply at low leaching time range, and became mild at high leaching time range. The recovery of titanium, vanadium, iron and aluminum could increase from 74.58%, 57.23%, 70.98% and 62.87% to 81.36%, 66.72%, 78.42% and 71.64% with increasing leaching time from 30 min to 60 min. However, those were 84.95%, 70.42%, 82.94% and 77.21% at 120 min.

3.6. Leaching mechanism with phase analysis

The XRD pattern of the leached red mud is depicted in Fig. 9 under the conditions of citric acid of 5%, sulfuric acid concentration of 5 mol/L, liquid to solid ratio of 5 mL/g, temperature of 90 ^oC and leaching time of 60 min.

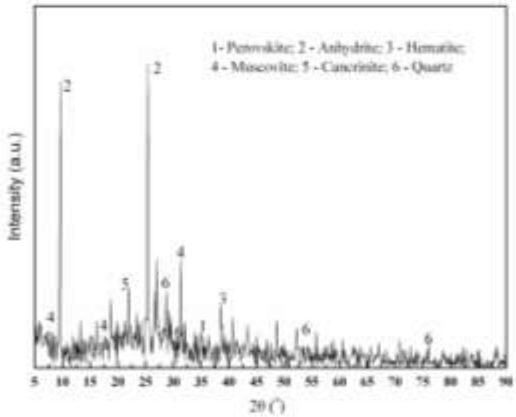

Fig. 9. The XRD pattern of the leached red mud with 5% citric acid.

It can be seen that perovskite, brookite and hematite have almost been dissolved by sulfuric acid with citric acid. Furthermore, cancrinite and muscovite were partly leached, whereas quartz was nearly not dissolved. The phase of calcite was disappeared and the phase of anhydrite was appeared. Therefore, the following chemical and phase reaction could be occurred according to the result.

$CaTiO_3 + H_2SO_4 \rightarrow H_2TiO_3 + CaSO_4 \downarrow$ (1)

$TiO_2 + H_2SO_4 \rightarrow TiO_3^{2-} + H^+ + SO_4^{2-}$ (2)

$Fe_2O_3 + H_2SO_4 \rightarrow Fe^{3+} + SO_4^{2-} + H_2O$ (3)

$K(Al,V)_2[OH]_2\{AlSi_3O_{10}\} + H_2SO_4 \rightarrow VOSO_4 + K^+ + Al^{3+} + SiO_3^{2-}$ (4)

$Na_2O(CaO)\cdot mSiO_2\cdot nAl_2O_3 + H_2SO_4 \rightarrow Al^{3+} + Na^+ + Ca^{2+} + SO_4^{2-} + SiO_2$ (5)

The titanium, vanadium, iron and aluminum could be dissolved into sulfuric acid solution from solid phase. However, the effect of citric acid during the acid leaching process was analyzed by XRD. The result was shown in Fig. 10.

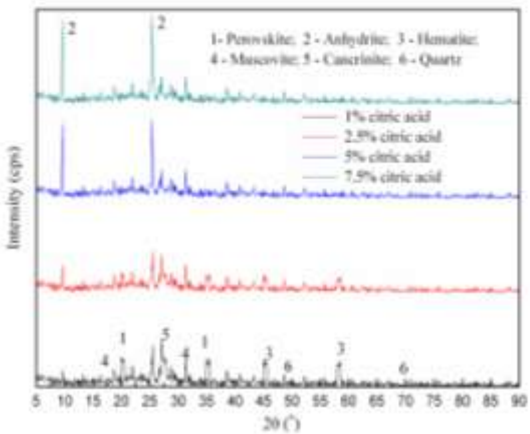

Fig. 10. The XRD pattern of the leached red mud

with different citric acid.

It can be seen that the citric acid could accelerate the dissolution of perovskite, brookite, hematite, cancrinite and muscovite, which increased the recovery of titanium, vanadium, iron and aluminum with increasing citric acid.

IV. CONCLUSIONS

The results obtained in the present work showed that titanium, vanadium, iron and aluminum could be in-depth leached with citric acid from red mud. The sulfuric acid concentration and liquid to solid ratio have been decreased with using citric acid in the acid leaching process. The main factors on recovery of valuable metals such as sulfuric acid concentration, leaching temperature and liquid to solid ratio from red mud were investigated. The recovery of titanium, vanadium, iron and aluminum reached 86.31%, 71.43%, 83.74% and 77.97% respectively under the conditions of sulfuric acid concentration of 5 mol/L, citric acid of 5%, liquid to solid ratio of 5 mL/g, temperature of 90 ^{o}C and time of 60 min. The dissolution of perovskite, brookite, hematite, cancrinite and muscovite resulted in the recovery of titanium, vanadium, iron and aluminum from red mud, which could be accelerated with using citric acid by the analysis of XRD.

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