Stripping of titanium from TBP-decanol phase

X H Mao
College of Biological and Chemical Engineering, Panzhihua University, Panzhihua 617000, Sichuan, China
Email: chdmaoxh@sina.com

Abstract. The stripping of titanium from TBP-decanol phase with hydrochloric acid has been investigated. The results showed that the stripping rate of titanium increased with decreased hydrochloric acid concentration in the aqueous phase, decreased organic and aqueous phase ratio and increased stripping temperature. Extracted titanium was easy to strip and 0.5 mol/L hydrochloric acid was a suitable stripping agent. The kinetics of the stripping process was fast, since the equilibrium was reached in 10 minutes. The extraction and stripping isotherms showed that through extraction and stripping titanium (IV) was separated and enriched as about five fold. The simulated extraction and stripping of titanium (IV) in leaching solution of blast furnace slag were proceeded.

1. Introduction
Hydrochloric acid method was reported by Altair for the manufacture of nano-TiO₂ [1]. The advantage of hydrochloric acid method is the low cost titanium raw material and less waste. In China the content of TiO₂ reaches 20-22% in the blast furnace slag smelted from vanadium-titanium magnetite, which comprehensive utilization is an urgent problem. The blast furnace slag has poor leaching performance and high impurity content. Hydrochloric acid method is with strong leaching and process flexibility of extraction operation. Therefore hydrochloric acid method is suitable for the extraction of titanium in blast furnace slag.

The extraction separation is the key process of hydrochloric acid method. In Altair process titanium was separated by extraction with TRPO as the extraction agent. However TRPO is expensive and poor to phase disengagement [2, 3].

A lot examination has been made for the extraction of titanium. The main extractants are acidic organophosphorus extractants and neutral organophosphorus extractants. But the extraction equilibrium time of titanium by acidic organophosphorus extractants is long (30-120 minutes) [4-6]. Neutral organophosphorus extractants including of TRPO, TOPO and TBP have been studied respectively for the extraction of titanium [7-13]. Among these studies the extraction of titanium (IV)
with mixed extractants of TBP and decanol, TOPO and decanol was reported [7]. As the addition of decanol the extraction yield of titanium increases largely. At the same time the synergistic extraction of metals has been investigated [14-15]. However the stripping behavior of titanium form TBP-decanol phase haven’t been studied.

In the present study the stripping of titanium from TBP-decanol phase was studied. The potential of TBP-decanol for the separation and recovery of titanium from hydrochloric leaching solutions of titanium slag has been assessed.

2. Experimental

2.1. Materials
Titanium (IV) solutions were prepared from TiCl₄. TBP and decanol were provided from AODA Chemical Co., Ltd. Other chemicals were of analytical reagent grade.

2.2. Methods
Solvent extraction experiments were conducted by mixing aqueous and organic phases under the certain conditions. After phase separation, the following methods were used to determine the concentration of the metal ions in the aqueous phase. Titanium (IV) was analyzed by spectrophotometry with hydrogen peroxide. Titanium (IV), calcium (II), magnesium (II) and aluminum (III) in the hydrochloric leaching solutions of titanium slag were analyzed by ICP. The concentration of the metal ions in the organic phase was obtained by mass balance.

3. Results and discussion

3.1. Extraction of titanium (IV) by TBP and decanol
The extraction of titanium in the acid chloride solutions was studied with TBP and decanol. And the extraction conditions were optimized on the basis of the relevant report [7]. The results showed that with the increasing of extractants total concentration the extraction rate of titanium (IV) first increased and then unchanged (Figure 1), with the increasing of the extraction temperature the extraction percentage of titanium (IV) decreased, with the increasing of the O/A the extraction rate of titanium (IV) increased and the concentration of titanium (IV) in the organic phase decreased, titanium (IV) in the acid chloride solutions could be extracted mostly by TBP and decanol within 10 minutes. And that the suitable extraction conditions was that using 1.0 mol/L TBP and 0.67 mol/L decanol as the extractant, with O/A equal to 1, 25°C extraction temperature and 10 minutes extraction time.
Based on the above results extraction isotherm has been obtained for a solution containing 0.15 mol/L titanium (IV) in 8 mol/L hydrochloric acid with 1.0 mol/L TBP and 0.67 mol/L decanol in kerosene as extraction agent (Figure 2). The result showed that the concentration of titanium (IV) in aqueous phase was below 0.02 mol/L in three or four stages at O/A equal to 1.

Figure 1. Effect of TBP-decanol concentration on the extraction of titanium (IV).

X-Extraction rate of titanium (IV)

3.2. Stripping of titanium

3.2.1. Choice of stripping agent. To realize the separation and recovery of titanium (IV) the stripping behavior of titanium from TBP-decanol phase has been studied with hydrochloric acid as the stripping agent (Figure 3).

The results showed that with the increase of hydrochloric acid concentration the stripping rate of titanium decreased. When using 0.5 mol/L hydrochloric acid as the stripping agent, the stripping
percentage of titanium was above 90%.

Figure 3. Stripping of titanium from TBP-decanol phase with HCl.

Y-Stripping rate of titanium

3.2.2. Effect of O/A. In the case of stripping by 0.5 mol/L hydrochloric acid the influence of stripping O/A was studied (Figure 4). The results showed that an increase in the O/A led to an increase in the stripping percentage of titanium and a decrease in the titanium concentration in stripping solutions. The suitable stripping O/A was 5.

Figure 4. Effect of the phase radio on the stripping of titanium.
3.2.3. Effect of stripping temperature. The impact of stripping temperature on the stripping of titanium was examined. The result showed that with the increase of the stripping temperature the stripping percentage of titanium increased slightly (Figure 5). The related stripping reaction is then endothermic. And the suitable stripping temperature was room temperature.

![Figure 5. Effect of temperature on the stripping of titanium.](image)

3.2.4. Effect of stripping time. Titanium in TBP-decanol phase was mixed with 0.5 mol/L hydrochloric acid for 1-30 minutes. The stripping percentage of titanium was above 90% within 10 minutes (Figure 6). From the result it was found that the stripping of titanium with 0.5 mol/L hydrochloric acid was a quick process, suitable to industrial application.

![Figure 6. Effect of stripping time on the stripping of titanium.](image)

3.2.5. Stripping isotherm. Based on these results, a stripping isotherm for titanium (IV) was obtained from a organic phase containing 0.15 mol/L titanium with 0.5 mol/L hydrochloric acid as stripping agent. A McCabe-Thiele plot (Figure 7) of titanium stripping showed that the concentration of titanium in stripping phase was below 0.01 mol/L in four stages with A/O equal to 1:5.
3.3. Extraction and separation of titanium (IV) from leaching solutions of titanium slag

The developed method was applied for the separation and recovery of titanium (IV) from the hydrochloric leaching solutions of titanium slag with 1.0 mol/L TBP and 0.67 mol/L decanol as extraction agent. As it is well known that ferric iron can be extracted selectively with TOA, in the present study the hydrochloric leaching solutions of titanium slag firstly was extracted to separate ferric iron by TOA.

Simulated counter-current extraction and stripping were made at laboratory scale at 298 K. The process comprised the steps of (1) extraction separation of ferric iron by TOA, (2) selective extraction of titanium (IV) from the iron raffinate in three stages of counter-current extraction (O/A = 1/1) with the mixed solvent system and (3) stripping of titanium in organic phase with 0.5 mol/L HCl in four stages (A/O = 1/5) to recover titanium. Through the concentration determination by ICP the results of the process were given in Table 1. The present investigations revealed that the mixed solvent system can be used as a selective extractant for the separation and recovery of titanium (IV) in the hydrochloric leaching solutions of titanium slag. Titanium (IV) was separated and concentrated through the process.

Table 1. Extraction and separation of titanium (IV) in the leaching solutions of titanium slag.

|               | Fe (mol/L) | Ti (mol/L) | Mg (mol/L) | Al (mol/L) | Ca (mol/L) |
|---------------|------------|------------|------------|------------|------------|
| Feed          | 0.02697    | 0.151857   | 0.1986     | 0.2716     | 0.4868     |
| Raffinate of Fe | 0.00161    | 0.152079   | 0.1988     | 0.2712     | 0.4858     |
| Raffinate of Ti | ——         | 0.008732   | 0.2128     | 0.3169     | 0.5535     |
| Strip solution of Ti | ——         | 0.568839   | 0.0027     | 0.0009     | 0.0313     |
4. Conclusion

The mixed extraction agent of TBP and decanol is effective and selective for the extraction of titanium (IV) in acidic chloride solutions. The extracted titanium (IV) is easy to strip and the stripping process is fast. The suitable stripping condition was that using 0.5 mol/L hydrochloric acid as stripping agent, with A/O equal to 1:5, 25°C stripping temperature and 10 minutes stripping time. Extraction and stripping isotherms were generated. The concentration of titanium (IV) in aqueous phase was below 0.02 mol/L in three or four stages with O/A equal to 1. The concentration of titanium (IV) in stripping phase was below 0.01 mol/L in four stages with A/O equal to 1:5. The extraction and stripping of titanium (IV) in leaching solution of blast furnace slag were proceeded.

References

[1] Zhang W, Zhu Z and Cheng C Y 2011 Hydrometallurgy 108(3) 177-188
[2] Reddy M L P and Saji J 2002 Miner. Process Extr. M. 23(3-4) 199-227
[3] Zhu Z W, Zhang W S and Cheng C Y 2011 Hydrometallurgy 105(3) 304-313
[4] Da Silva G C, Da Cunha J W D, Dweck J and Afonso J C 2008 Miner. Eng. 21(5) 416-419
[5] Saji J, John K S and Reddy M L P 2000 Solvent. Extr. Ion. Exc 18(5) 877-894
[6] Awwad N S and Ibrahim H A 2013 J. Environ. Chem. Eng. 1(1-2) 65-72
[7] Allal K M, Hauchard D, Stambouli M, Pareau D and Durand G 1997 Hydrometallurgy 45(1) 113-128
[8] EI Dessouky S I, EI Nadi Y A, Ahmed I M, Saad E A and Daoud J A 2008 Chem. Eng. Process 47(2) 177-183
[9] Narayanan R P and Lakshmipathy R M 2004 J. Chem. Technol. Biotechnol. 79(7) 734-741
[10] Saji J and Reddy M L P 2001 Hydrometallurgy 61(2) 81-87
[11] Saji J K, Saji J, Reddy M L P, Ramamohan T R and Rao T P 1999 Hydrometallurgy 51(1) 9-18
[12] Seyfi S and Abdi M 2009 Miner. Eng. 22(2) 116-118
[13] Hao X L, Lv L, Liang B, Li C, Wu P and Wang J 2012 Hydrometallurgy 113-114(3) 185-191
[14] Zhang Y, Zhang T A, Lv G Z, Zhang G Q, Liu Y and Zhang W G 2016 Hydrometallurgy 166 87-93
[15] Zhao Z G, Baba Y, Kubota F, Kamiya N and Goto M 2014 J. Chem. Eng. Japan 47(8) 656-662