Reductive Stripping of Fe(III)

Bull. Korean Chem. Soc. **2014**, Vol. 35, No. 7   2109

Stripping of Fe(III) from the Loaded Mixture of D2EHPA and TBP with Sulfuric Acid Containing Reducing Agents

Yang Liu, Sang-Ho Nam,[†] and Manseung Lee[*]

Department of Advanced Material Science & Engineering, Institute of Rare Metal, Mokpo National University, Channam 534-729, Korea. [*]E-mail: mslee@mokpo.ac.kr
[†]Department of Chemistry, Mokpo National University, Chonnam 534-729, Korea

Solvent extraction of Fe(III) from chloride solution by using a mixture of D2EHPA (Di-(2-ethylhexyl)-phosphoric acid) and TBP (Tri-butyl phosphate) and the reductive stripping of Fe(III) from the loaded organic were investigated. Quantitative extraction of Fe(III) from the solution (Fe concentration = 90 g/L) was accomplished in two cross-current extraction stages by using the mixture of D2EHPA and TBP. In order to facilitate the stripping efficiency, a reductive stripping method was employed by using H_2SO_3 or Na_2SO_3 as a reducing agent. The addition of H_2SO_4 into reducing agents led to improvement in the stripping efficiency while high concentration acid would suppress it. Both of the mixtures of $H_2SO_4 + H_2SO_3$ and $H_2SO_4 + Na_2SO_3$ showed good efficiency for the stripping of Fe(III), while the latter was recommended as the stripping solution based on the economics and experimental condition.

Key Words : Iron, Mixture of D2EHPA and TBP, Reductive stripping, Sulfurous acid, Sodium sulfite

Introduction

In the recovery of valuable metals from ores by hydro-metallurgical method, leaching of the ores with hydrochloric acid solution usually results in a solution with high concentration of ferric iron. Thus, removal or recovery of ferric iron from the leaching solution is of importance in hydrometallurgy. Several processes are available to remove ferric iron from chloride-rich solution, such as precipitation and solvent extraction. In the case of precipitation, some of valuable metals would be co-precipitated with Fe(III) during the precipitation, which would decrease the recovery percentage of these metals. Compared to precipitation, solvent extraction has certain advantages. Ferric iron has a strong tendency to form complexes with chloride ion which can be extracted selectively by amines[1,2] and TBP.[3-5] Moreover, there is some difference in the value of pH_{50} (the pH at which 50% of the metal is extracted) by cationic extractants[6-9] among Co(II), Fe(III), Mn(II) and Ni(II).[10] In the case of separation of ferric iron by amines or TBP, strong HCl solution is needed, while moderate acidity is enough to selectively extract ferric iron by cationic extractants.[1,5,8]

Among the extractants mentioned above, extraction of Fe(III) by D2EHPA has been extensively investigated. Difficulties have been reported in the stripping of Fe(III) from the loaded D2EHPA even with concentrated acid.[11,12] An alternative method to overcome this difficulty has been developed by employing the mixture of D2EHPA and TBP for the extraction of Fe.[13-16] It was found that the mixture of D2EHPA and TBP exhibited better extraction ability than single extractant[13,14] and the stripping of Fe(III) from the mixture of D2EHPA and TBP was easier than that from D2EHPA alone.[15,16] Although the use of mixture of D2EHPA and TBP

can increase the extraction and stripping efficiency of Fe, it is still difficult to strip most of Fe when the concentration of loaded iron is high.

Stripping of ferric iron may be improved by reducing the activity of ferric iron in the aqueous phase. One way to decrease the activity of ferric ion in the aqueous phase is to reduce ferric to ferrous ion by adding some reducing agents.[17] Gaseous reductants, such as SO_2[17] and H_2[18] have been explored. However, the reductive stripping by using gaseous reductants has some problems due to the necessity of employing high pressure and temperature. In order to increase the stripping efficiency of Fe with high concentration from the loaded mixture of D2EHPA and TBP, sulfurous acid and sodium sulfite were employed as a reducing agent. In this work, the effect of the concentration of acid and reducing agent on the stripping of ferric iron has been investigated and an optimum condition to strip ferric iron is proposed.

Experimental Procedures

Reagents and Solution. Di-2-ethylhexyl phosphoric acid (D2EHPA, 95%) was obtained from Daihachi Chemical industry Co., Ltd., Japan. Tri-butyl phosphate (TBP, 98%) was purchased from Yakuri chemicals, Japan. Kerosene supplied by DaeJung Chem, Korea was used as a diluent. All the organic were used without any purification.

A synthetic chloride solution with 90 g/L ferric iron was employed in the experiments. The synthetic solution was prepared by dissolving $FeCl_3 \cdot 6H_2O$ (Yakuri, Japan) in deionized water water. HCl and NaOH were used to adjust the solution pH to a desired value. Sulfurous acid solution (H_2SO_3, 5%) and sodium sulfite (Na_2SO_3, 96%), were used as reducing reagents, which were purchased from Junsei

Chem, Japan and DaeJung Chem, Korea, respectively. The concentration of sulfurous acid was 0.6 M.

Procedure. All extraction and stripping experiments were performed with the desired volume of aqueous and organic solution in screwed cap bottle and the mixture was shaken for 30 min by using Wrist Action Shaker (Burrell, Model 75). The concentration of the elements in raffinate was analyzed by ICP-AES (OPTIMA 4300 DV). The pH of the solution was measured with an Orion Star A211 pH meter. The metal concentration in the organic was obtained by mass balance. All experiments were carried out at ambient temperature.

Results and Discussion

Extraction of Fe(III) by the Mixture of D2EHPA and TBP. Since D2EHPA is a cationic extractant with weak acidity (pK_a = 3.01), the acidity of the solution should be decreased for ferric iron to be extracted and thus the pH of the resulting solution was increased to 1 by adding NaOH solution. Solvent extraction experiments of ferric iron were done by employing the mixture of D2EHPA and TBP. For this purpose, the concentration of D2EHPA was fixed at 1 and 1.5 M and the concentration of TBP in the mixture was varied from zero to 1.5 M. The addition of TBP enhanced the iron extraction and the extraction efficiency of Fe(III) increased with the increase in the concentration of D2EHPA and TBP (see Fig. 1). With the mixture of 1 M D2EHPA and 1 M TBP, 50% of Fe(III) were extracted. About only 10% increase in the extraction percentage of iron was observed with the mixture of 1.5 M D2EHPA and 1 M TBP. During
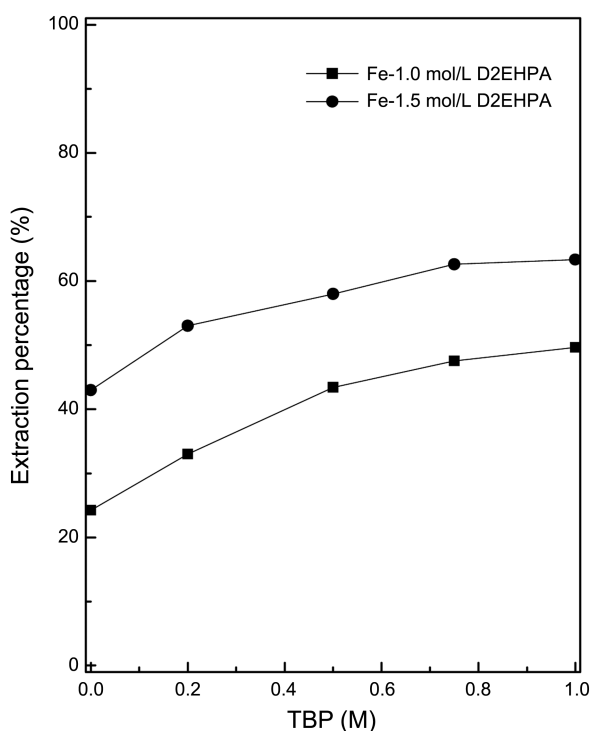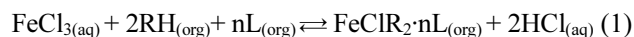
the extraction with the mixture of 1.5 M D2EHPA and 1 M TBP, solidification in the organic phase occurred. Therefore, the mixture of 1 M D2EHPA and 1 M TBP was employed in further experiments. In our experimental range, the solvent extraction reaction of iron by the mixture of D2EHPA (RH) and TBP (L) can be represented as[13,14]:

$$FeCl_{3(aq)} + 2RH_{(org)} + nL_{(org)} \rightleftharpoons FeClR_2 \cdot nL_{(org)} + 2HCl_{(aq)} \quad (1)$$

Since the extraction percentage of iron by using the mixture of 1 M D2EHPA and 1 M TBP was only 50%, multistage extraction is needed to extract all of the iron present in the leaching solution. In order to determine the number of theoretical stages, a McCabe-Thiele diagram for cross-current extraction[19] was constructed at O/A = 3. In these experiments, the concentration of D2EHPA and TBP in the mixture was kept at 1 M, respectively. The resulting diagram for Fe(III) extraction is shown in Figure 2, indicating that the concentration of Fe(III) would be decreased to 1.0 g/L (corresponding to the cumulative extraction percentage of 98.7%) after two cross current stages at an O/A ratio of 3.

In order to verify the prediction of the McCabe-Thiele diagram for the extraction of iron, a cross-current extraction was employed at an O/A ratio of 3. The extraction percentage of Fe(III) in each stage is shown in Table 1. The cumulative extraction percentage of Fe(III) was 94.78% and 99.99%, respectively for each stage. The final concentration of Fe(III) in the raffinate after two cross-current stages was 5 mg/L. It can be concluded that the mixture of D2EHPA and TBP is efficient for the extraction of Fe(III) from the leach solution.
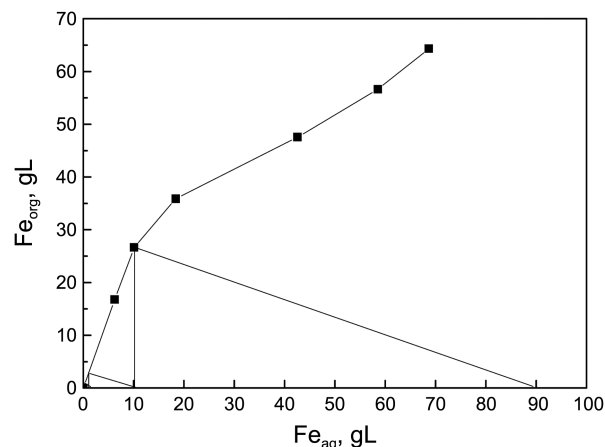

Figure 1. Effect of the concentration of TBP and D2EHPA on the extraction of Fe(III) from the solution.

Figure 2. Diagram for the extraction of iron from the solution by the mixture of D2EHPA and TBP. [D2EHPA] = 1 M, [TBP] = 1 M, [Fe^{3+}] = 90 gl/L, O/A = 3:1.

Table 1. The percentage extraction in each stage of cross-current extraction of Fe(III) by using 1 M D2EHPA mixed with 1 M TBP at the O/A ratio of 3

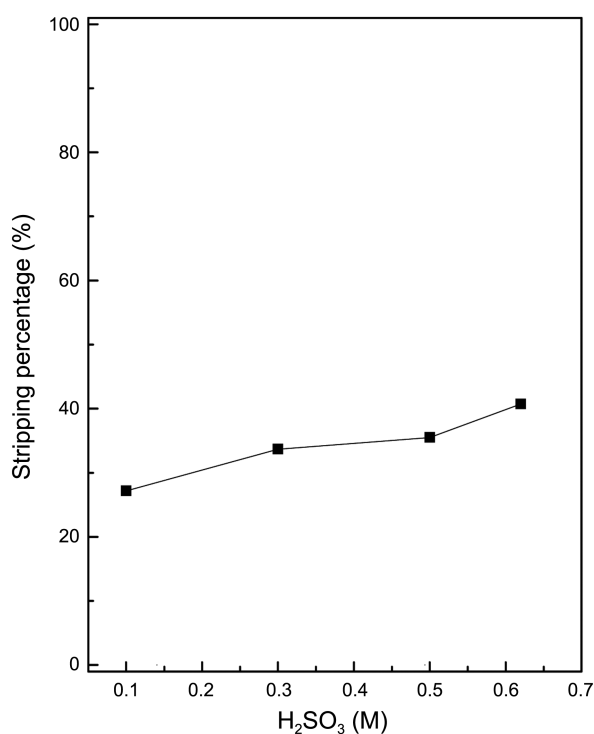|	Fe-conc. (mg/L)	Fe-% EX	
Leach solution	89900		
SX-stage 1-raf	4692	94.78	99.99
SX-stage 2-raf	4.98	99.89	

Figure 3. Effect of H_2SO_3 concentration on the stripping of Fe(III) from the loaded mixture of 1 M D2EHPA and 1 M TBP.

Stripping of Fe(III) from the Loaded Mixture of D2EHPA and TBP by using Single Sulfurous Acid. The concentration of iron in the loaded mixture of 1 M D2EHPA and 1 M TBP after single stage extraction at an O/A ratio of 3 was found to 28.5 g/L. First, HCl was tested for the stripping of Fe(III) from the loaded organic. The stripping percentage of Fe(III) increased from 30% to 43% with an increase in HCl concentration from 1 to 3 M. Further increase of acid concentration resulted in a decrease in the stripping percentage. The decrease in stripping percentage might be ascribed to the back-extraction of iron due to the high concentration of acid in the strip solution. When HCl was employed as a stripping agent, stripping of ferric iron from the mixture of D2EHPA and TBP was more plausible than that from D2EHPA alone. However, it was difficult to strip most of the iron in the loaded mixture of D2EHPA and TBP because the concentration of iron in the organic was high. The stripping reaction of Fe(III) from loaded mixture of D2EHPA and TBP may be described as follows:

$$FeClR_2 \cdot nL_{(org)} + 2H^+_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + 2RH_{(org)} + nL_{(org)} \quad (2)$$
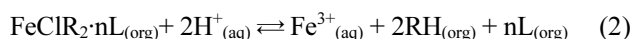
The decrease in Fe(III) activity could shift the equilibrium of Eq. (2) toward right and the stripping extent would be increased. A method to decrease the activity of Fe(III) is to reduce Fe(III) to Fe(II). In order to reduce the activity of ferric iron in the stripping solution by reduction to ferrous, sulfurous acid solution was used as a stripping agent. The concentration of sulfurous acid solution was adjusted from 0.1 to 0.6 M. Figure 3 illustrates the effect of H_2SO_3 concentrations on the stripping of Fe(III) from the loaded mixture of D2EHPA and TBP. It is obvious that the stripping

percentage increased with increasing H_2SO_3 concentration and about 40% stripping of iron was obtained by 0.6 M sulfurous acid. Compared to the stripping of iron by HCl, employment of sulfurous acid as a stripping agent did not lead to much improvement in the stripping efficiency of iron. The advantage of sulfurous acid over hydrochloric acid lies in the fact that a lower concentration of sulfurous acid (0.6 M) resulted in the same stripping percentage of iron by 3 M HCl solution.

Stripping of Fe(III) from the Loaded Mixture of D2EHPA and TBP by using the Mixture of Sulfurous and Sulfuric Acid. In the stripping of iron by sulfurous acid, ferric iron stripped into the sulfurous acid is reduced to ferrous in the aqueous phase. Since sulfurous acid is a weak acid and the optimum concentration of sulfurous acid was low, a strong acid solution is needed to enhance the stripping of Fe(III) from the loaded organic. The reduction of Fe(III) to Fe(II) by sulfurous acid leads to the oxidation of sulfite to sulfate ion. The employment of sulfuric acid could avoid the introduction of other anion. Therefore, a mixture of sulfuric and sulfurous acid was tested to strip iron from the mixture of D2EHPA and TBP. For this purpose, sulfuric acid concentration in the acid mixture was varied from zero to 3 M by keeping the concentration of sulfurous acid at 0.5 M. The stripping percentage of Fe was increased from 40 to 72% when the concentration of H_2SO_4 was increased to 2 M (Fig. 4). Further increase of sulfuric acid concentration to 3 M resulted in only 2% increase in stripping percentage of iron. When H_2SO_4 was used as a stripping reagent in the presence
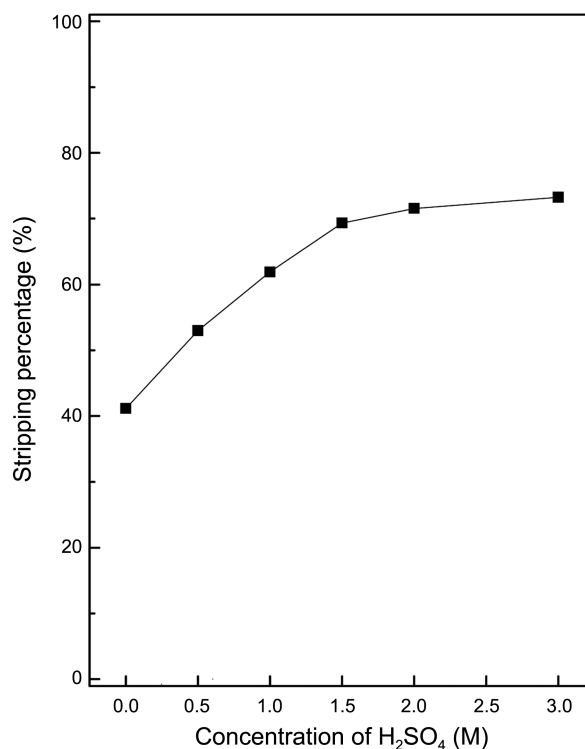

Figure 4. Effect of H_2SO_4 concentration in the mixture with 0.5 M H_2SO_3 on Fe(III) stripping from the loaded mixture of 1 M D2EHPA and 1 M TBP.
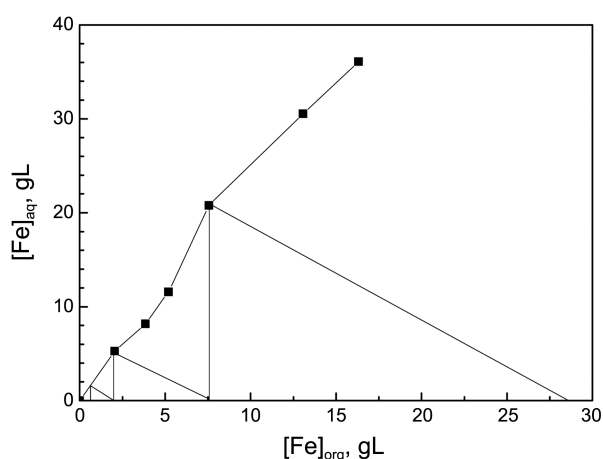
Figure 5. Diagram for the stripping of Fe(III) from the loaded mixture of D2EHPA and TBP by the mixture of H_2SO_4 and H_2SO_3. $[H_2SO_4]$ = 2 M, $[H_2SO_3]$ = 0.5 M, $[Fe(III)]$ = 28.5 g/L, A:O = 1:1.

of H_2SO_3, the stripping percentage was greatly improved. Therefore, a mixture of 2 M H_2SO_4 and 0.5 M H_2SO_3 was chosen as a suitable stripping solution for iron from the loaded mixture of D2EHPA and TBP.

A McCabe-Thiele diagram for the stripping of iron with the mixture of 2 M H_2SO_4 and 0.5 M H_2SO_3 was constructed at an A/O ratio of 1 in order to predict the number of theoretical stages. The McCabe-Thiele diagram shows that 3 stages are required for the stripping of iron at an A/O ratio of 1 by cross-current stripping (see Fig. 5). In order to verify the prediction by the stripping diagram, stripping experiments of iron from the loaded organic (D2EHPA + TBP) by the mixture of 2 M H_2SO_4 and 0.5 M H_2SO_3 were carried out in cross-current tests. In cross-current stripping experiments, the stripping percentage of iron in the second stage was only 20% by the mixture of 2 M H_2SO_4 and 0.5 M H_2SO_3. The decrease in the stripping percentage of iron in the second stage of cross-current stripping might be related to the fact that the acidity of the stripping solution was not strong enough to strip the iron. Therefore, further experiments have been carried out in two stages by varying the concentration of sulfuric acid from 2 to 5 M, while increasing the concentration of sulfurous acid to 0.6 M. The results of these experiments are shown in Table 2. In the first stage, the stripping percentage of Fe(III) by 2 M and 3 M H_2SO_4 was similar, but decreased with the further increase of H_2SO_4 concentration above 3 M. The decrease in the stripping percentage of iron at higher concentration of sulfuric acid may be explained by the overall oxidation-reduction reaction (Eq. (3)) occurring in the stripping solution containing sulfurous acid.

$$2Fe^{3+} + H_2SO_3 + H_2O \rightleftharpoons 2Fe^{2+} + 4H^+ + SO_4^{2-} \qquad (3)$$
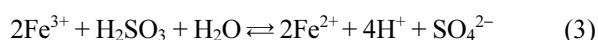
Eq. (3) indicates that the concentration of sulfate ion in the stripping solution increases as the reduction of ferric iron by sulfurous acid proceeds. Therefore, presence of high concentration of sulfate ion in the stripping solution has adverse effect on the reduction of ferric iron. Hence, the decrease in

Table 2. Stripping of Fe by using H_2SO_4 mixed with H_2SO_3

Stripping reagent	% strip		
	First stage	Second stage	Total
2 M H_2SO_4 + 0.6 M H_2SO_3	76.4	57.7	90.0
3 M H_2SO_4 + 0.6 M H_2SO_3	76.0	100	100
4 M H_2SO_4 + 0.6 M H_2SO_3	65.9	77.8	92.4
5 M H_2SO_4 + 0.6 M H_2SO_3	53.5	45.4	74.7

the stripping percentage of iron at higher concentration of sulfuric acid is due to the depression of the reduction reaction of ferric iron.

In the second stage, the stripping percentage was first increased from 58 to 100% with increasing H_2SO_4 concentration from 2 to 3 M and then decreased. The decrease in the stripping percentage might be ascribed to either the depression of the reduction reaction or back-extraction of iron due to the high concentration of acid in the strip solution. Although the increase of sulfurous acid concentration to 0.6 M increased the stripping slightly in the first stage, the stripping percentage increased sharply in the second stage compared to that by using 0.5 M sulfurous acid. Complete stripping was obtained at the second stripping stage by using the mixture of 3 M H_2SO_4 and 0.6 M H_2SO_3. This result implies that the concentration of sulfurous acid is more important than that of sulfuric acid for the stripping and 0.6 M sulfurous acid should be supplied in the continuous experiments to strip most of iron completely. Our data suggest that stripping of Fe(III) from the loaded organic can be achieved by using the mixture of 0.6 M H_2SO_3 mixed with 3 M H_2SO_4 in two stages.

Stripping Fe(III) from the Loaded Mixture of D2EHPA and TBP by using the Mixture of Sodium Sulfite and Sulfuric Acid. The weight percentage of sulfurous acid in market is low and thus the highest concentration of sulfurous acid is just 0.6 M, which restricts the reducing and stripping action of sulfurous acid. Sodium sulfite is also a strong reducing agent which could be used for the reduction of Fe(III). In order to investigate the possibility of using sodium sulfite in the stripping of ferric iron as a reducing agent, single sodium sulfite solution was employed for the stripping and reduction of Fe(III). The concentration of sodium sulfite was varied from 0.1 to 1.0 M. The stripping percentage of iron was negligible, indicating that the reduction

Table 3. Stripping of Fe by using H_2SO_4 mixed with Na_2SO_3

Stripping reagent	% strip		
	First stage	Second stage	Total
0.1 M Na_2SO_3 + 3 M H_2SO_4	75.1	73.8	92.6
0.3 M Na_2SO_3 + 3 M H_2SO_4	77.5	74.1	93.3
0.5 M Na_2SO_3 + 3 M H_2SO_4	76.4	56.4	88.2
0.7 M Na_2SO_3 + 3 M H_2SO_4	75.0	41.6	83.4
1 M Na_2SO_3 + 3 M H_2SO_4	71.2	29.7	77.4

reaction of Fe(III) occurred in aqueous phase after stripping. Therefore, adding acid to the sodium sulfite is necessary to strip ferric iron. Therefore, 3 M H_2SO_4 was added to the reducing agent solution as a stripping reagent while varying the concentration of Na_2SO_3 from 0.1 to 1 M. The experiments were also carried out in two cross current stages. In the first stage, the stripping percentage of iron was 75% and the concentration of Na_2SO_3 affected little the stripping of iron. In the second stage of cross current stripping experiments, the stripping percentage of iron was decreased with increasing Na_2SO_3 concentration. During the preparation of the mixture of Na_2SO_3 and sulfuric acid, sulfur dioxide gas was evolved when the concentration of sodium sulfite was high. The following equation could represent the evolution of sulfur dioxide gas between Na_2SO_3 and sulfuric acid.

$$Na_2SO_3 + H_2SO_4 \rightleftharpoons Na_2SO_4 + H_2O + SO_2 \qquad (4)$$

Therefore, the decrease in the stripping percentage may be ascribed to the consumption of Na_2SO_3 and H_2SO_4 during the preparation of stripping solution. After two stages of cross current stripping, the maximum stripping percentage obtained by using the mixture of 0.1 M Na_2SO_3 and 3 M H_2SO_4 was 93%.

Both 3 M H_2SO_4 + 0.6 M H_2SO_3 and 3 M H_2SO_4 + 0.1 M Na_2SO_3 are sufficient to quantitatively strip ferric iron from the loaded mixture of D2EHPA and TBP in two or three stages. The purity of H_2SO_3 is very low while the price is a little higher compared to Na_2SO_3. Since the economics of solvent extraction process depends on the selection of reagents, it is necessary to select a cheap reagent for the recovery of metals from the organic. Therefore, the mixture of sulfuric acid and sodium sulfite was recommended for the stripping solution of iron from the loaded D2EHPA and TBP on the basis of the economics of the proposed process.

Conclusions

The extraction of Fe(III) from chloride solution by using the mixture of D2EHPA and TBP and stripping from the loaded organic by using H_2SO_4 mixed with H_2SO_3 or Na_2SO_3 as a reducing agent were studied. Extraction data indicated that TBP enhanced the extraction percentage of Fe(III) in the presence of D2EHPA. A mixture of 1 M D2EHPA and 1 M TBP was used to increase extraction percentage and to facilitate stripping. Two stages of cross-current extraction with the above mixture at an O/A ratio of 3 led to complete extraction of iron from the solution where the concentration of iron was 90 g/L. The concentration of iron in the raffinate was only 5 mg/L.

In order to increase the stripping efficiency, the reductive stripping of iron (28.5 g/L) with the mixture of reducing reagent (H_2SO_3 and Na_2SO_3) and H_2SO_4 has been investigated. Single H_2SO_3 could only strip 40% iron from the loaded organic, which might be ascribed to low acidity of H_2SO_3 solution. The stripping efficiency was increased by adding H_2SO_4 to sulfurous acid solution. Since the oxidation product of H_2SO_3 or Na_2SO_3 is sulfate, suppression of the reduction reaction occurred when the concentration of H_2SO_4 was high. Stripping experiments indicated that the mixture of 3 M H_2SO_4 + 0.6 M H_2SO_3 led to complete stripping of iron from the loaded organic, while two cross-current stripping with the mixture of 3 M H_2SO_4 + 0.1 M Na_2SO_3 resulted in 93% stripping. Based on the economics and experimental condition, the mixture of 3 M H_2SO_4 and 0.1 M Na_2SO_3 was recommended for the stripping solution of ferric iron from the loaded organic mixture of D2EHPA and TBP.

References

 1. Lee, M. S.; Lee, K. J. *Hydrometallurgy* **2005**, *80*, 163.
 2. Mishra, R. K.; Rout, P. C. *et al. Hydrometallurgy* **2011**, *108*, 93.
 3. Reddy, B. R.; Sarma, P. V. R. B. *Hydrometallurgy* **1996**, *43*, 299.
 4. Saji, J.; Reddy, M. L. P. *Hydrometallurgy* **2001**, *61*, 81.
 5. Lee, M. S.; Lee, G. S. *et al. Mater. Trans.* **2004**, *45*, 1859.
 6. Roddy, J. W.; Coleman, C. F. *et al. J. Inorg. Nucl. Chem.* **1971**, *33*, 1099.
 7. Sato, T.; Nakamura, T. *et al. Hydrometallurgy* **1985**, *15*, 209.
 8. Biswas, R. K.; Begum, D. A. *Hydrometallurgy* **1998**, *50*, 153.
 9. Stefanakis, M. I.; Monhemius, A. J. *Hydrometallurgy* **1985**, *15*, 113.
10. Aguilar, M.; Cortina, J. L. *Solvent Extraction and Liquid Membranes: Fundamentals and Applications in New Materials*; CRC Press: New York, USA, 2008; p 155.
11. Yu, S. Q.; Chen, J. Y. *Hydrometallurgy* **1989**, *22*, 267.
12. Akhlaghi, M.; Rashchi, F. *et al. International Mineral Processing Congress*; QLD: Brisbane, 2010; Sep. Australia
13. Sahu, K. K.; Das, R. P. *Metall. Mater. Trans. B* **1997**, *28*, 181.
14. Sahu, K. K.; Das, R. P. *Metall. Mater. Trans. B* **2000**, *31*, 1169.
15. Hirato, T.; Wu, Z. *et al. Hydrometallurgy* **1992**, *28*, 81.
16. Singh, D. K.; Mishra, S. L. *et al. Hydrometallurgy* **2006**, *81*, 214.
17. Majima, H.; Izaki, T. *Metall. Mater. Trans. B* **1985**, *16*, 187.
18. Demopoulos, G. P. *Hydrometallurgy* **1984**, *12*, 299.
19. Rydberg, J.; Cox, M. *et al. Solvent Extraction Principles and Practice, Second Edition* 2004, M. Dekker, Inc. Press.