

Separation of Fe(III) and Al via Tributyl Phosphate and 2-Octanol in the Comprehensive Recovery Process of Metals from Hydrochloric Acid Leaching Solution of Fly Ash

Xiaozhou ZHOU, Yujun SHEN*, Jun PENG and Qiang LIU

Changsha Research Institute of Mining and Metallurgy Co., LTD, Changsha 410086, PR China

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The extraction of Fe(III), Al(III), Zn(II), Pb(II), Cu(II) and Hg(II) from hydrochloric acid leaching solution of fly ash by using solvent extraction with 25% (v/v) tributyl phosphate (TBP), 35% (v/v) 2-octanol and 40% (v/v) kerosene was investigated. To achieve the separation of Fe(III) from Al(III), Zn(II), Pb(II), Cu(II) and Hg(II), five-stage counter-current batch simulation test was conducted under the conditions of O/A = 2/1, 25°C, 5 min, 3.66 mol/L of HCl, resulting in the extraction efficiencies of Fe(III) as 99.86%; and the separation coefficients, e.g. $\beta_{\text{Fe/Al}}$, $\beta_{\text{Fe/Zn}}$, $\beta_{\text{Fe/Pb}}$, $\beta_{\text{Fe/Cu}}$, $\beta_{\text{Fe/Hg}}$ were $\sim\infty$, 1.7×10^4 , 1.8×10^4 , 2.1×10^4 , 6.7×10^3 , respectively; in addition, over 99.9% of Fe(III) could be stripped in a six-stage counter-current batch simulation test using 0.1 mol/L HCl. The mechanism of Fe(III) extraction using tributyl phosphate and 2-octanol was discussed according to FT-IR spectra results.

1. Introduction

Coal is the primary fossil energy resource in China and is mainly used in electric power generation. Large quantities of coal that contains abundant Al, Li, Ga, and REY (REE+Y) have been found in many mining districts located in northern Shanxi Province [1] and in the middle-western region of Inner Mongolia, China [2]. These metals can be further enriched during the combustion process, and most of them are transferred to coal ash. High-alumina fly ash (HAFA) can be utilized as a substitute for bauxite for Al production [3]. At present, most studies about extracting valuable metals from HAFA use the fly ash from pulverized coal (PC) furnaces as raw material [4]. However, an increased amount of HAFA discharge from circulating fluidized bed (CFB) boilers are observed every year in main coal producing areas, including Shanxi province and Inner Mongolia in Northern China. Resources are wasted if CFB-derived HAFA is only used to produce building materials because CFB-derived HAFA contains large amounts of Al and other rare elements. Recycling these valuable metals from CFB-derived HAFA would not only conserve natural resources and reduce environmental impacts but also achieve ash utilization with high economic benefits.

The operating temperature of a CFB boiler is 800-950°C, which is much lower than that of a PC furnace. The combustion temperature greatly affects the mineral transformation during the formation of coal fly ash. In contrast to the PC-derived HAFA, all of Al in CFB-derived HAFA is evidently amorphous [5]. The direct acid leaching activity of these amorphous components is higher than that of crystalline components in PC-derived HAFA, because the chemical structure (Si-O-Al bonds) of amorphous components is more active than that of crystal minerals [6]. A one-step hydrochloric acid leaching process to treat CFB-derived

HAFAs have been independently developed by Shenhua Zhungeer Energy and Resources Comprehensive Development Co., Ltd. A proposed process is as follows: CFB-derived HAFAs leached with hydrochloric acid, removal of Fe(III) by resin adsorption, removal of Ca, crystallization of aluminum chloride and production of Al₂O₃. In the process of removal of iron by resin, almost all iron, gallium, a large number of heavy metals and a small amount of aluminum in the leachate are also absorbed together. After hydrochloric acid desorption, the desorbed solution is used to extract gallium. The residual solution after gallium extraction mainly contains Fe ~100 g/L, Al ~12 g/L, hydrochloric acid 40 – 50 g/L, and a small amount of heavy metals such as Zn, Cu, Pb, Hg, etc.

To realize resource utilization and recycling of the waste water, first, iron and aluminum are devised to be separated, and heavy metals are removed secondarily. Precipitation [7], adsorption [8], ion exchange [9] and solvent extraction [10] are the traditional separation methods of Fe(III). Solvent extraction has the advantages of convenient operation, mild reaction condition, good selectivity, high recovery rate and product of high purity [11,12]. The study on iron removal of aluminum sulfate with low iron content is with the largest number, and the extraction system also has a variety of choices. Acidic organophosphorus esters such as P204 [13], amine extractants such as tertiary amine Alamine 336 [14], carboxylic acid extractants such as Versatic 10 acid [15] and neutral organophosphorus reagents such as TBP [16] have been studied for iron separation. Sun [17] investigated the separation of ferric ions from aluminum sulfate using N235 and P204, and the reported iron removal and stripping percentages were >97% and 99%, respectively. The extraction system consisting of the primary amine N1923, 2-octanol and kerosene removed 99.99% of iron from industrial aluminum sulfate as an iron(III) hydroxyl-sulfate complex at pH > 1.2 [18].

The typically studied solvent extraction systems are composed of neutral organophosphorus and high concentration of hydrochloric acid. The mixture of 70% (v/v) TBP and 30% (v/v) MIBK [19-21] has been extensively researched because of its faster phase separation and large extraction capacity. However, there are few studies have described the separation of iron from aluminum chloride with high iron(III) content using TBP in detail. In the present study, TBP was used to separate iron from a high iron- and certain aluminum concentration solution; 2-octanol, a more economical and common modifier, was employed to replace MIBK, it sufficiently solved the three-phase and emulsification problems of TBP.

2. Experimental

2.1 Reagents

TBP (99%), 2-octanol (99%) and sulfonated kerosene were provided by Shanghai Rare Earth Chemical Co., Ltd., China. Hydrochloric acid of analytical purity was supplied by Kelong Chemical Corporation. The chemical composition of feed liquid was shown in Table 1. The HCl concentration in the feed liquor was 1.08 mol/L. The concentrations of iron and aluminum in the solution were respectively 102.61g/L and 12.81g/L. In addition, it also contained a certain amount of heavy metal ions. The H⁺ concentration of the solution was modified by adding hydrochloric acid.

Table 1. Concentration of metal ions in the solution.

Metals	Fe(III)	Al(III)	Zn(II)	Pb(II)	Cu(II)	Hg(II)
Content, mg/L	102610	12810	146.15	29.83	36.53	3.38

2.2 Procedure and analyses

In all extraction tests, the aqueous solution and the organic solution were placed in a 125-mL separating funnel; then, the funnel was placed in a thermostatic water bath at a certain temperature and oscillated; subsequently, kept static; after phase separation, 1 mL of the aqueous phase was sampled for analysis.

The concentrations of Al, Zn, Pb, Cu, and Hg in the aqueous phase were determined by a Thermo iCAP 7000 inductively coupled plasma optical emission spectrometer (ICP-OES). The concentrations of Fe were determined by the potassium dichromate ($K_2Cr_2O_7$) volumetric method, and the concentrations of ions in the loaded organic phase were obtained by mass balance calculations. The acid content in the aqueous solution was determined by potentiometric titration with aqueous NaOH. The total element analysis of the strip liquor was determined by ICP with mass spectrometric detection (ICP-MS). A Nicolet iS50 instrument was applied to obtain the IR spectrums of organic phase. The ion extraction efficiency was calculated by Eq. (1), where E denoted the extraction efficiency (%) of the ion, V_0 and V_1 represented, respectively, the volume of the aqueous phase before and after extraction, and C_0 and C_1 were the concentrations of the ion in the aqueous phase before and after extraction, respectively. The ion stripping efficiency was calculated by Eq. (2), where S denoted the stripping efficiency of the ion, V_{org} and V_2 represented, respectively, the volumes of the loaded organic phase and strip liquor, and C_{org} and C_2 were the ion concentrations of the loaded organic phase and strip liquor, respectively. The ion distribution ratio was calculated by Eq. (3), D denoted distribution ratio of the ion. $\beta_{Fe/Me}$ denoted the separation coefficient of Fe(III) to Me in the extraction, which was calculated using Eq. (4).

$$E = 100\% \times (C_0V_0 - C_1V_1) / C_0V_0 \quad (1)$$

$$S = 100\% \times C_2V_2 / C_{org}V_{org} \quad (2)$$

$$D = 100\% \times C_{org} / C_1 \quad (3)$$

$$\beta_{Fe/Me} = [E_{Fe} / (1 - E_{Fe})] / [E_{Me} / (1 - E_{Me})] \quad (4)$$

Me represented Al, Zn, Pb, Cu, and Hg in Eq. (4)

3. Results and Discussion

3.1 Solvent extraction of Fe(III)

3.1.1 The synergistic extraction of TBP and 2-Octanol

The influence of different extraction systems on the extraction of Fe(III) was investigated, and the results are shown in Table 2. Under the experiment conditions, the corresponding distribution ratio was up to 0.98 in the TBP and 2-octanol system, which was greater than the sum (0.59) of distribution ratio in the systems of others. The result showed that the mixture of TBP and 2-octanol had obvious synergistic extraction effect on the extraction of Fe(III), and $\beta_{Fe/Al}$ also increased obviously. Meanwhile, 2-octanol had the ability of adjusting the polarity of the organic phase which avoided the generation of a third phase; thus, no third phase was observed in 2-octanol based- or synergistic extraction system, that agreed well with Zhou *et al.*'s report [22].

3.1.2 Effect of TBP concentration

The tests for investigating the effect of TBP concentration (10 – 30% (v/v)) on the extraction of Fe(III), Al, Zn, Pb, Cu, and Hg were carried out. The results, shown in Figure 1, illustrated that the extraction of Fe(III)

rapidly increased from 50.5% to 69.23% with TBP concentration ranging from 10% to 25%. Further increased the concentration of TBP, the extraction efficiency of Fe(III) increased slightly. The extractions of Zn, Pb and Hg were below 1.6% with 25%(v/v) TBP. The Cu and Al extraction percentages were negligible in these experiments.

Table 2. Extraction results of Fe(III) with different extraction systems.

System	$D_{\text{Fe(III)}}$	$\beta_{\text{Fe/Al}}$	Experimental phenomenon
TBP	0.29	41.21	A third phase appeared
2-octanol	0.30	14.08	Without third phase
TBP and 2-octanol	0.98	7.5×10^3	Without third phase

Note: TBP, 25%(v/v); 2-octanol, 35%(v/v); TBP and 2-octanol, 25%(v/v) and 35 %(v/v); O/A = 2; contact time = 5 min; HCl concentration = 3.66 mol/L; temperature = 25°C.

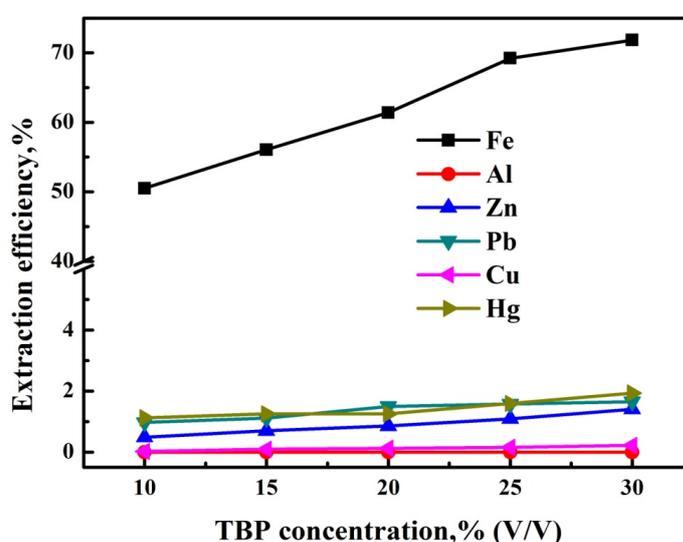


Figure 1. Effect of TBP concentration on the extraction of metal ions (O/A phase ratio = 2/1, contact time = 5 min, 2-octanol concentration = 35%(v/v), HCl concentration = 3.66 mol/L, temperature = 25°C).

3.1.3 Effect of HCl concentration

Figure 2 showed the effect of HCl concentration on the extraction of Fe(III), Al, Zn, Pb, Cu, and Hg. With HCl concentration increasing from 2.8 mol/L to 4.1 mol/L, the extractions of Fe(III) increased from 56.70% to 75.16%. The extractions of Zn, Pb and Hg varied very little. The Cu and Al extraction percentages were negligible in these experiments. This meant that organic affinity of iron-chlorine complex was greater than that of others. Meanwhile, the higher the concentration of hydrochloric acid was, the higher the extraction rate of iron that could be achieved. However, the concentration of hydrochloric acid should not be too high, there were two main reasons: (1) high concentration of HCl in aqueous phase increased consumption of hydrochloric acid. (2) stripping was the inverse process of extraction, more HCl would be brought into organic phase from a stronger acidity aqueous phase in extraction process, and the acidity of stripping solution would be further increased, a lower iron stripping efficiency would be finally observed. Therefore, the concentration of hydrochloric acid of aqueous phase must be appropriate.

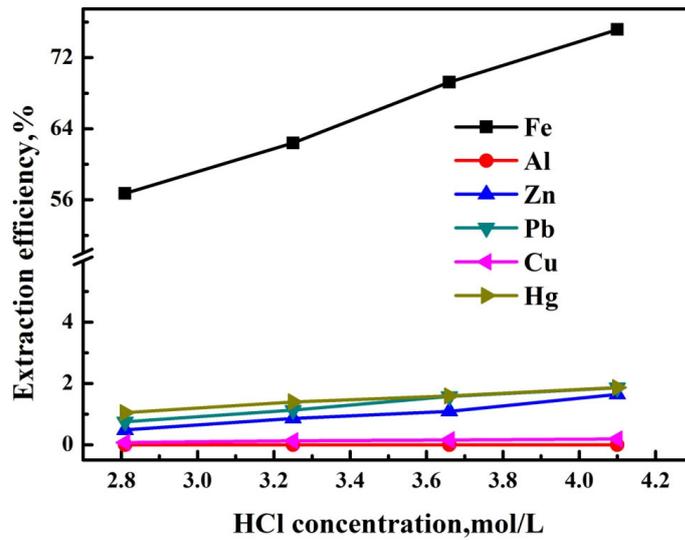


Figure 2. Effect of HCl concentration on the extraction of metal ions (O/A phase ratio = 2/1, contact time = 5 min, 25%(v/v) TBP and 35%(v/v) 2-octanol in sulfonated kerosene, temperature = 25°C).

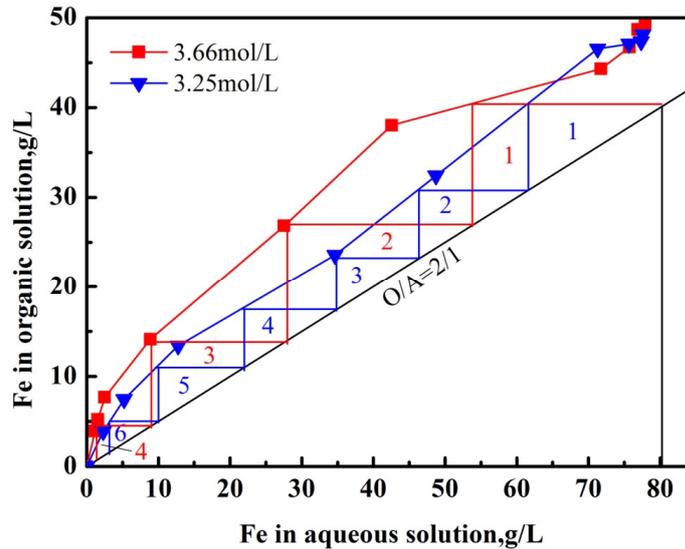


Figure 3. The extraction equilibrium isotherm of Fe(III) (contact time = 5 min, temperature = 25°C, 25%(v/v) TBP and 35%(v/v) 2-octanol in sulfonated kerosene).

3.1.4 Extraction equilibrium isotherm of Fe (III)

The Fe(III) extraction equilibrium isotherm was obtained by varying the O/A phase ratio from 20/1 to 1/20, with an organic phase consisting of 25% (v/v) TBP and 35% (v/v) 2-octanol in sulfonated kerosene in the presence of different HCl concentration, as shown in Figure 3. The saturated capacity of Fe³⁺ extraction reached 48.09 g/L and 49.27 g/L in the presence of 3.25 and 3.66 mol/L hydrochloric acid, respectively. McCabe-Thiele analysis predicted that the concentration of Fe(III) in the raffinate can be reduced to less than 1.5 g/L by adopting a four-stage and six-stage continuous counter current extraction at an O/A ratio of 2/1 in the HCl concentration of 3.25 mol/L and 3.66 mol/L, respectively. In the actual operation process, due to stage efficiency, 1-2 more stages were generally added on the basis of the theoretical series. To confirm this,

a five-stage and seven-stage counter-current batch simulation test were carried out under different HCl concentrations. The results are shown in Table 3. The extraction of Fe (III) were 98.34% and 99.86% in the presence of 3.25 mol/L and 3.66 mol/L hydrochloric acid, respectively. The result of 3.66 mol/L HCl is shown in Table 4. The separation coefficients of Fe(III) over Al, Zn, Pb, Cu, Hg were $\sim\infty$, 1.7×10^4 , 1.8×10^4 , 2.1×10^4 , 6.7×10^3 , respectively.

Table 3. The result of multistage counter-current batch simulation test under different HCl concentration after equilibrium.

HCl concentration, mol/L	Stage number	Fe ³⁺ in raffinate, mg/L	Extraction, %
3.25	seven	1330	98.34
3.66	five	130	99.86

Note: contact time = 5 min, temperature = 25°C, 25%(v/v) TBP and 35%(v/v) 2-octanol in sulfonated kerosene, O/A = 2/1.

Table 4. The result of five-stage counter-current batch simulation test of 3.66 mol/L HCl after equilibrium.

Solution concentration/ separation coefficient/ extraction	Elements					
	Fe(III)	Al(III)	Zn(II)	Pb(II)	Cu(II)	Hg(II)
Feed solution, mg/L	80240	10020	114.29	23.33	28.57	2.64
Loaded organic, mg/L	35350		2.18	0.43	0.46	0.12
Raffinate, mg/L	130	12030	137.41	10.53	34.13	2.84
$\beta_{\text{Fe/Me}}$	1	$\sim\infty$	1.7×10^4	1.8×10^4	2.1×10^4	6.7×10^3
Extraction, %	99.86	~ 0	4.33	4.15	0.43	10.46

Note: contact time = 5 min, temperature = 25°C, 25%(v/v) TBP and 35%(v/v) 2-octanol in sulfonated kerosene, O/A = 2/1; Me represented Al, Zn, Pb, Cu, and Hg; the volume of raffinate was less than that of feed solution.

3.2 Stripping

3.2.1 Stripping equilibrium isotherm of Fe(III)

The stripping equilibrium isotherm of Fe(III) from the loaded organic phase of 3.66 mol/L HCl using 0.1 mol/L HCl was obtained by varying the O/A phase ratio from 20/1 to 1/20. The McCabe-Thiele diagram for the stripping of Fe(III) was shown in Figure 4. Five stripping stages using an O/A phase ratio of 2.6/1 leads to quantitative stripping of Fe(III) from the loaded organic. In the actual operation process, considering stage efficiency, 1 – 2 more stages were generally added on the basis of the theoretical series. To confirm this, a six-stage counter-current batch simulation test was conducted under present conditions and the typical stripped organic and strip liquor were sampled and analyzed. For the strip liquor and stripped organic contented 91.52 g/L and 0.021 g/L of iron, respectively, the stripping efficiency was over 99.9%. The total element analysis of the strip liquor is listed in Table 5. With low impurity content and high ferric chloride concentration, the strip liquor can be directly applied to synthesize ferric oxide red or polyferric chloride.

Table 5. The total element analysis of the strip liquor.

Element	Fe	Al	Na	Mg	K	Ca
Content, mg/L	91520	7.2	11.3	0.50	17.0	11.0
Element	Mn	B	Mo	Pb	Zn	
Content, mg/L	1.40	0.31	2.29	2.48	1.05	

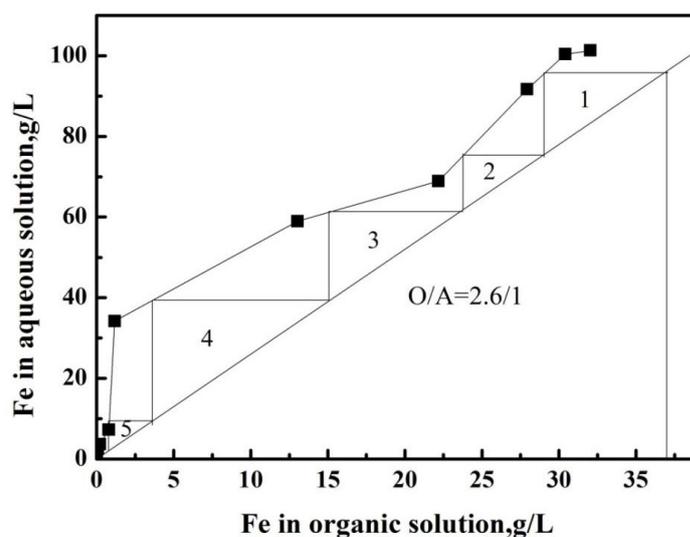


Figure 4. The stripping equilibrium isotherm of Fe(III) (contact time = 5 min, temperature = 25°C, stripping agent: 0.1 mol/L HCl).

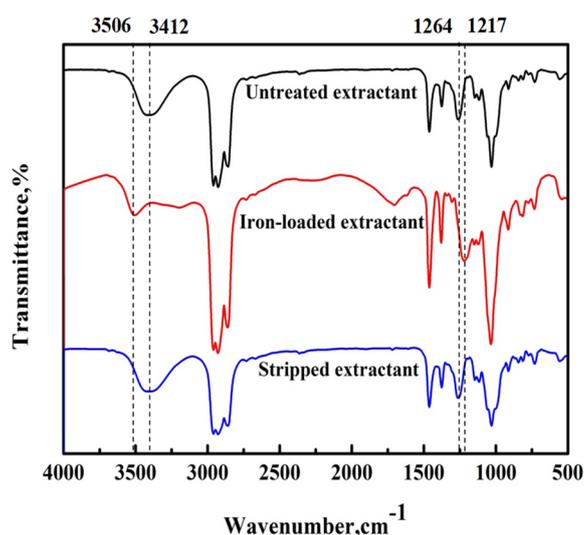


Figure 5. IR spectra for iron-loaded, untreated and stripped extractants.

3.3 Analysis of IR spectra

To reveal the interaction between the extractant and Fe(III), the FT-IR spectra of new organic phase (25% TBP, 35% 2-octanol, and 40% kerosene(v/v)), Fe(III) loaded organic phase, and regenerated organic phase after stripping were recorded. The spectra of extractants and their complexes with iron are shown in Figure 5, and the peaks obtained in different spectra were given in Table 6.

It can be seen that the peak at 1264 cm⁻¹, which was attributed to the stretching vibration of the P=O group in TBP, changed after extraction, indicating that the phosphoryl oxygen atom coordinated with the solute during the extraction process. The peaks at 1217 cm⁻¹ in TBP were attributed to the stretching vibration of P=O·HFeCl₄. 2-Octanol also displayed little extractability. The absorption peak at 3412 cm⁻¹ caused by the O-H stretching vibration of 2-octanol shifted to 3506 cm⁻¹ of iron loaded extractant, and this result was attributed to the vibration of -OH·HFeCl₄. The spectrum of stripped extractant was identical to that of

untreated extractant which confirmed the complete stripping of iron from the loaded extractant. This was consistent with results of the extraction of Fe(III) with TBP and 2-octanol from hydrochloric acid media [23-25].

Table 6. Characteristic IR spectral data for untreated, iron-loaded and stripped extractants.

Probable assignment	Wavenumber, cm ⁻¹		
	Untreated extractant	Iron-loaded extractant	stripped extractant
ν C-H	2960	2959	2960
$\delta^{\text{as}}\text{CH}_3$ -, $\delta^{\text{s}}\text{CH}_3$ -	1461, 1375	1461, 1378	1461, 1375
$\nu^{\text{as}}\text{-CH}_2$ -, $\nu^{\text{s}}\text{-CH}_2$ -	2927, 2858	2928, 2862	2927, 2858
ν P-O-C	1029	1033	1029
ν P=O	1264	1217	1264
ν O-H	3415	3506	3412
$\nu^{\text{as}}\text{ C-O}$	1116	1122	1116

3.4 The flowsheet for separation of Fe(III) and aluminum

A flow sheet for extraction and separation of Fe(III) and Aluminum from hydrochloric acid leaching solution of fly ash by using the TBP–2-Octanol mixed extractant was proposed as in Figure 6. In this technology route, iron was extracted by 25% TBP and 35% 2-octanol (v/v) with high recovery ratio and good selectivity. Iron was then effectively stripped using 0.1 mol/L HCl. The ferric chloride solution with negligible impurities was obtained after stripping. Raffinate was returned to the main process for aluminum recovery after removing heavy metals.

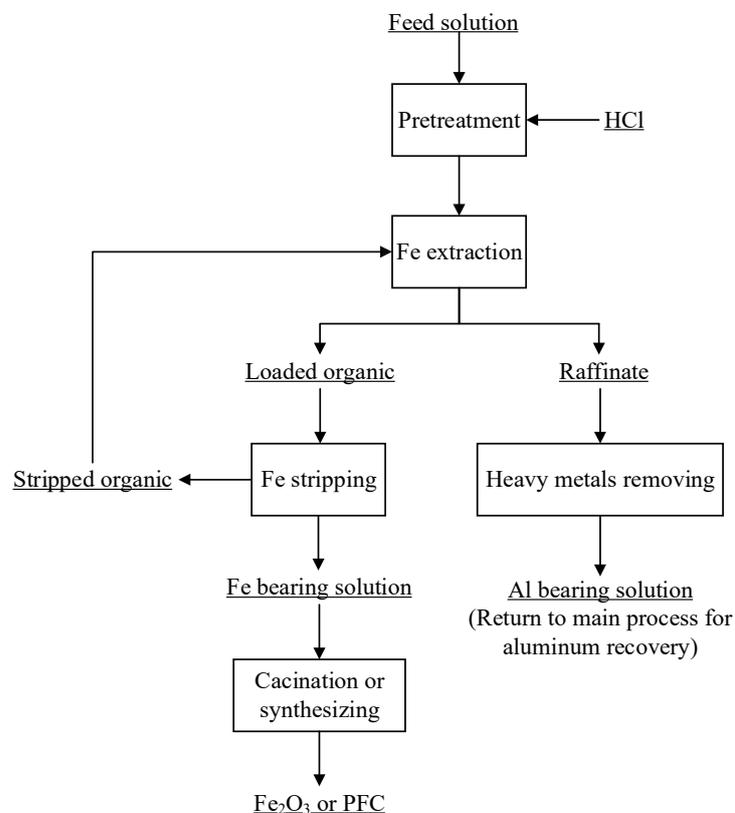


Figure 6. Flow sheet for separation of Fe(III) and Al.

4. Conclusions

(1) The mixture of TBP and 2-octanol had a positive synergistic extraction effect on the extraction of Fe(III) from HCl based solution; meanwhile, it was an effective extractant for the selective separation of iron from hydrochloric acid leaching solution of fly ash leaching with high content of aluminum and certain amount of heavy metals. The result of FT-IR spectra indicated the mechanism of iron extraction using TBP and 2-octanol extractant.

(2) The separation coefficients, e.g. $\beta_{\text{Fe}/\text{Al}}$, $\beta_{\text{Fe}/\text{Zn}}$, $\beta_{\text{Fe}/\text{Pb}}$, $\beta_{\text{Fe}/\text{Cu}}$, $\beta_{\text{Fe}/\text{Hg}}$ were $\sim\infty$, 1.7×10^4 , 1.8×10^4 , 2.1×10^4 , 6.7×10^3 , respectively, in the five-stage counter-current batch simulation test.

(3) The loaded organic phase can be stripped completely and regenerated in a six-stage counter-current batch simulation test using a 0.1 mol/L HCl. With low impurity content and high ferric chloride concentration, the strip liquor could be used to synthesize ferric oxide red or polyferric chloride directly.

References

- 1) Y. Sun, C. Zhao, J. Zhang, J. Yang, Y. Zhang, Y. Yuan, J. Xu, D. Duan, *Energy Explor. Exploit.*, **31**, 727-744 (2013).
- 2) S. Dai, Y. Jiang, C. R. Ward, L. Gu, V. V. Seregin, H. Liu, D. Zhou, X. Wang, Y. Sun, J. Zou, D. Ren, *Int. J. Coal Geol.*, **98**, 10-40 (2012).
- 3) D. H. Xu, H. Q. Li, W. J. Bao, Y. Wang, *Hydrometallurgy*, **165**, 336-344 (2016).
- 4) H. Tanvar, S. Chauhan, N. Dhawan, *Mater. Today: Proc.*, **5**, 17055-17063 (2018).
- 5) Z. B. Ma, K. K. Chang, K. Z. Yan, P. H. Zhang, F. Q. Cheng, *Clean Coal Technol.*, **22**, 20-25 (2016).
- 6) C. B. Guo, J. J. Zou, C. D. Wei, Y. S. Jiang, *Energy Fuels*, **27**, 7868-7875 (2013).
- 7) K. Jae-Kyeong, O. Han-Sang, J. Chang-Wha, S. Yong-Jae, J. Hee-Dong, K. Kee-Kahb, *Chem. Eng. Res. Des.*, **88**, 1467-1473 (2010).
- 8) R. Navarro, V. Gallardo, I. Saucedo, E. Guibal, *Hydrometallurgy*, **98**, 257-266 (2009).
- 9) M. Bethan, D. David, *Hydrometallurgy*, **98**, 122-127 (2009).
- 10) R. K. Biswas, D. A. Begum, *Hydrometallurgy*, **50**, 153-168 (1998).
- 11) J. R. Kumar, J. S. Kim, J. Y. Lee, H. S. Yoon, *Sep. Purif. Rev.*, **40**, 77-125 (2011).
- 12) W. Wang, C. Y. Cheng, *J. Chem. Technol. Biotechnol.*, **86**, 1237-1246 (2011).
- 13) L. Li, S. Xu, Z. Ju, F. Wu, *Hydrometallurgy*, **100**, 41-46 (2009).
- 14) M. S. Lee, K. J. Lee, Y. J. Oh, *Mater. Trans.*, **45**, 2364-2368 (2004).
- 15) D. Pouillon, F. M. Doyle, *Hydrometallurgy*, **19**, 269-288 (1988).
- 16) R. K. Mishra, P. C. Rout, K. Sarangi, K. C. Nathsarma, *Hydrometallurgy*, **104**, 298-303 (2010).
- 17) X. Sun, Y. Sun, J. Yu, *Sep. Purif. Technol.*, **159**, 18-22 (2016).
- 18) M. Li, Z. He, L. Zhou, *Hydrometallurgy*, **106**, 170-174 (2011).
- 19) B. R. Reddy, P. V. Sarma, *Hydrometallurgy*, **43**, 299-306 (1996).
- 20) J. Saji, M. L. P. Reddy, *Hydrometallurgy*, **61**, 81-87 (2001).
- 21) K. Sarangi, P. K. Parhi, E. Padhan, A. K. Palai, K. C. Nathsarma, K. H. Park, *Sep. Purif. Technol.*, **55**, 44-49 (2007).
- 22) X. K. Zhou, Z. F. Zhang, S. T. Kuang, Y. L. Li, Y. Q. Ma, Y. H. Li, W. P. Liao, *Hydrometallurgy*, **185**, 76-81 (2019).

- 23) X. M. Wang, W. Z. Liu, B. Liang, L. Lü, C. Li, *Sep. Purif. Technol.*, **158**, 96-102 (2016).
- 24) S. I. El Dessouky, Y. A. El-Nadi, I. M. Ahmed, E. A. Saad, J. A. Daoud, *Chem. Eng. Proc.*, **47**, 177-183 (2008).
- 25) X. T. Yi, G. S. Huo, W. Tang, *Hydrometallurgy*, **192**, 105265 (2020).