Korean J. Chem. Eng., 39(12), 3442-3451 (2022)
DOI: 10.1007/s11814-022-1185-1

pISSN: 0256-1115
eISSN: 1975-7220

Effective separation of Zn, Fe, and Mn from roasting-water leaching solution of blast-furnace dust using a precipitation-solvent extraction process

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(*Received 4 April 2022 • Revised 20 May 2022 • Accepted 23 May 2022*)

Abstract−Selective extraction of Zn from blast furnace dust can be achieved by the ammonium sulfate roasting-water leaching process. An innovative method for effective separation of Zn, Fe, and Mn from roasting-water leaching solution of blast-furnace dust by precipitation-solvent extraction process is proposed in this research. The Fe of leaching solution was selectively converted into $FePO_4 \cdot 2H_2O$ precipitate by using Na_2HPO_4 as precipitant. The precipitation efficiency of Fe reached 99.17%, while that of Zn was only 0.20% under the solution pH of 2.2, molar ratio of Na_2HPO_4 to Fe of 1.2 : 1, reaction temperature of 30 °C, and reaction time of 50 min. The zinc in the filtrate was extracted with Cyanex 302, and Zn (99.94%) was extracted through two-stage countercurrent extraction under initial pH of 3.4, Cyanex 302 concentration of 25%, and O/A of 2 : 1. Subsequently, Zn (99.96%) of the organic phase was stripped using 0.75 mol/L sulfuric acid by one-stage countercurrent stripping. Furthermore, according to thermodynamic calculation, it is proved that extracting Zn from sulfuric acid solution with Cyanex 302 is an exothermic reaction. The proposed process flowsheet may be used to efficiently recover Zn and Fe from blast-furnace dust.

Keywords: Blast-furnace Dust, Na_2HPO_4 Precipitating, Cyanex 302, Zinc Extraction, Thermodynamics

INTRODUCTION

As a typical secondary zinc resource, the recycling of blast-furnace dust generated by the ironmaking process is attracting increasing attention [1-3]. It is mainly composed of zinc, iron, calcium, and magnesium, in which zinc content usually exceeds 5% [4]. According to statistics, in 2017, the global output of blast-furnace dust waste was approximately 1.2-2.0 billion tons [5]. Unfortunately, this hazardous waste is not suitable for building materials because of its non-ferrous metal content. Thus, blast furnace dust has not been reasonably utilized [6,7]. Discharging large quantities of blast-furnace dust can cause serious environmental problems [8]. Accordingly, it is crucial to apply appropriate technologies for effectively treating blast-furnace dust and utilizing it as a resource.

The valuable metal zinc in blast-furnace dust mainly exists in the form of zinc ferrite [9], so it is difficult to separate and recover zinc by traditional methods. To effectively recycle this waste, many pyrometallurgical [10-13] and hydrometallurgical [4,14,15] processes have been developed. In the process of hydrometallurgy, leaching zinc from blast-furnace dust requires high-temperature and high-concentration acid liquor [16]. Due to the large amount of iron leached out by hydrometallurgy, when zinc is recovered from the leaching solution, iron should be removed first, which will produce large amounts of iron-containing residues. The process of pyrometallurgy for the recovery of blast-furnace dust can be classified into two methods: direct reduction and smelting reduction [17]. Pyrometallurgy is more widely used because it can selectively extract target metals from blast-furnace dust and, at the same time, it is convenient for the downstream process to separate and recover metals [18].

Many researchers have made different researches on decomposing zinc ferrite and selectively extracting zinc by pyrometallurgical process, such as roasting blast-furnace dust with sodium carbonate and leaching with acid solution [19-22]. Roasting with $FeCl_3 \cdot 6H_2O$ has the same treatment effect on zinc ferrite [23]. In addition, it has been shown that zinc ferrite can be decomposed into ZnO and Fe_3O_4 by calcination of C or CO [24-26]. However, the above methods consume a large number of sodium ions, have high roasting temperature, and easy sintering [23,27,28]. Compared with the above methods, blast-furnace dust is leached out by water after roasting with ammonium sulfate, which can obtain higher zinc leaching efficiency with a slight amount of iron extraction, thus achieving the purpose of separating zinc from iron [16,29,30].

The leaching solution of blast-furnace dust obtained by ammonium sulfate roasting-water leaching process mainly contains rich valuable metal zinc and small amounts of iron, manganese, and magnesium impurities. Although a small amount of iron can be precipitated by adjusting pH, and then zinc can be extracted, because ferric hydroxide is flocculent precipitation, zinc will be adsorbed in the precipitation process. At present, solvent extraction [31-33] and neutralization precipitation [34] technology have become effective methods to recover metals from an acidic solution. However, the

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precipitation method not only consumes a large amount of neutralizer but also produces a large amount of useless solid waste, causing secondary pollution [35]. In contrast, solvent extraction has become one of the most effective extraction methods because of its high selectivity, high extraction efficiency, and low processing time and operation cost [36]. Numerous alkaline, acidic and neutral extractants have been investigated to extract zinc from acidic solutions [37-41], such as TBP, Cyanex 301, D2EHPA, and Alamine 336. Among them, acid organophosphorus Cyanex extractant is popular because of its poor water solubility and strong extraction ability [39,42,43]. Biswas et al. [44] reported that Cyanex 302 extracted Zinc and manganese separately. Cole et al. [45] observed that the order of extracting zinc, cobalt, and manganese cations with Cyanex 302 reagent was as follows: zinc>cobalt>manganese.

In the study, for effective separation of Zn, Fe, and Mn from roasting-water leaching solution of blast-furnace dust, the process of precipitating iron with Na_2HPO_4 and extracting zinc with Cyanex 302 extractant is proposed. The phosphate was innovatively used as a precipitant to selectively remove iron from the solution, and the technological conditions of selective precipitation of iron in sulfuric acid solution by Na_2HPO_4 were explored. The technological parameters of Cyanex 302 extraction to separate zinc from the filtrate after iron removal were determined, and the process conditions of stripping zinc directly from the Zn-loaded organic phase with sulfuric acid were explored. In addition, the thermodynamic behavior of zinc extraction from sulfuric acid media with the Cyanex 302 extraction system was systematically investigated. The whole separation process is relatively simple and may be effectively applied to the separation and recovery of zinc from roasting-water leaching solution of blast-furnace dust. Finally, based on optimizing the separation conditions, a flow chart of recovering zinc and iron from blast-furnace dust was put forward.

MATERIALS AND METHODS

1. Materials

Blast-furnace dust samples were provided by Baoshan Iron & Steel Co., Ltd. The Cyanex 272 extractant and sulfonated kerosene were all purchased from Shanghai McLean Biochemical Technology Co., Ltd. The inorganic chemical reagents used in the experiments are all analytical and purchased from Sinopharm Chemical Reagents Co., Ltd., without any purification treatment before use. The leaching solution used in this research was obtained by roasting-water leaching of blast-furnace dust with ammonium sulfate, which roasting condition was that the mass ratio of ammonium sulfate to blast-furnace dust was 8 : 5, roasting temperature was 650 °C, and roasting time was 80 min. The leaching efficiency of zinc reached 93.64% under the leaching temperature of 80 °C, mass ratio liquid to solid of 10 : 1, and leaching time of 30 min, while that of iron was only 6.87%. The main metal contents in the leaching solution are shown in Table 1.

Table 1. Main metal contents in the leaching solution

Element	Zn	Fe	Mn	Mg	SO_4^{2-}	pH
Concentration (g/L)	5.47	2.64	1.78	0.09	24.47	0.38

2. Experiment Procedures

2-1. Removal of Iron Experiments

The removal of iron experiments were carried out on a magnetic stirrer. 100 mL leaching solution was put into a 250 mL conical flask, then a certain amount of Na_2HPO_4 was added, and the pH of the solution was adjusted to a predetermined value with 1 mol/L H_2SO_4 solution or 1 mol/L NaOH solution. Finally, the conical flask was put into a water bath beaker on a magnetic stirrer to react at a certain temperature for some time. After the reaction, filtering to obtain filtrate and filter residue. The concentration of iron, zinc, and other metals in the filtrate was determined by an inductively coupled plasma optical emission spectrometer (ICP-OES: Optima 7300V, Perkin-Elmer, America). The precipitation efficiency of the metal is calculated according to Eq. (1) below.

$$\eta=\frac{CV-C_oV_o}{CV}\times 100\% \tag{1}$$

where C and V represent that metal concentration and volume in the solution participate in the precipitation reaction, respectively; C_o and V_o are the metal concentration and volume in the filtrate obtained after the precipitation reaction, respectively.

2-2. Extraction of Zinc Experiments

The filtrate obtained from the removal of iron under the best conditions was used as raw material for the extraction of zinc experiments. Before solvent extraction, the pH of the solution was adjusted with 1 mol/L H_2SO_4 solution or 1 mol/L NaOH solution. The organic phase (preparation of Cyanex 302 and kerosene) and solution were added to the separatory funnel. After a period of mechanical vibration, the two phases were completely separated. The experiment on the influence of extraction temperature on zinc extraction efficiency was carried out on an electrically heated magnetic stirrer. After the mixture of the solution and organic phase was added to the triangular flask, it was put into the water bath beaker in the electrically heated magnetic stirrer and stirred at the preset temperature for a certain time through the magnetic rotor. After that, it was poured into a separatory funnel for phase separation. The sulfuric acid solution was used as a stripping agent for stripping zinc from the Zn-loaded organic phase. Metals concentrations in raffinate and stripping solution were determined by ICP-OES. Based on the ion concentration in the aqueous phase before and after extraction, extraction efficiency (E), distribution ratio (D), separation factor (β), and stripping efficiency (S) were calculated by Eqs. (2)-(4), respectively.

$$E=\frac{C_{org}V_{org}}{C_{org}V_{org}+C_{aq}V_{aq}}\times 100\% \tag{2}$$

$$D=\frac{C_{org}}{C_{aq}} \tag{3}$$

$$\beta=\frac{D_a}{D_b} \tag{4}$$

$$S=\frac{C'_{aq}V'_{aq}}{C'_{org}V'_{org}}\times 100\% \tag{5}$$

where V_{aq} and C_{aq} are the volume of the aqueous phase and metals concentration in the extraction process, respectively; V_{org} and C_{org}

represent the volume of organic phase and metals concentration in the extraction process, respectively; D_a and D_b refer to the distribution ratios of elements a and b, respectively; V'_{aq} and C'_{aq} refer to the volume of stripping solution and metals concentration in the stripping process, respectively; V'_{org} and C'_{org} are the volume of loaded organic phase and metals concentration in the stripping process, respectively.

RESULTS AND DISCUSSION

1. Species Distribution of Metal Ions in the Leaching Solution

Fig. 1 displays the species distribution of 5.47 g/L Zn, 2.64 g/L Fe, 1.78 g/L Mn and 0.09 g/L Mg in sulfuric acid solution (24.47 g/L SO_4^{2-}) with the change of pH. Fig. 1(a) indicates that Zn^{2+} is the main existing form of zinc in strongly acidic solution, and with the increase of pH, zinc is gradually transformed into the form of $Zn(SO_4)_2^{2-}$. The zinc in the leaching solution will be transformed into $Zn(OH)_2$ precipitate under a pH higher than 7. Note that at a pH higher than 12, part of $Zn(OH)_2$ precipitates are gradually transformed into $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$, $Zn_2(OH)_6^{2-}$ and re-dissolved in the solution. Fig. 1(b) displays the species distribution of 2.64 g/L Fe in sulfuric acid solution (24.47 g/L SO_4^{2-}) with different pH. As seen that iron mainly exists in the forms of $FeHSO_4^{2+}$, $FeSO_4^+$ and $Fe(SO_4)_2^-$ at a pH of 0-3 due to the concentration of SO_4^{2-} is much higher than that of Fe^{3+} in the leaching solution. Only when the pH is above 3.3, the iron in the solution will be transformed into $Fe(OH)_3$ precipitate. Fig. 1(c) shows that when the pH is lower than 7.8, manganese exists as Mn^{2+} in the solution. As pH increases further, $Mn_2(OH)_3^+$ ions are observed at pH above 7.8, while manganese is gradually transformed into $Mn(OH)_2$ precipitation at pH above 9.2. Fig. 1(d) explains that when the pH is lower than 9.5, the magnesium in the leaching solution exists in the form of Mg^{2+}, while magnesium is gradually converted to $Mg(OH)_2$ precipitation at pH above 9.5.

Based on the above analysis, theoretically, although iron in leaching solution can be converted into $Fe(OH)_3$ precipitate by adjusting pH, $Fe(OH)_3$ precipitate is an amorphous floc, which not only adsorbs a large amount of zinc but also is difficult to filter. Therefore, the removal of iron should avoid this method as much as possible to simplify the industrialization process and improve the recovery efficiency of zinc.

2. Selective Removal of Fe with Na_2HPO_4

We tried using Na_3PO_4 as a precipitant in the beginning, but since Na_3PO_4 is too alkaline, using it as a precipitant would greatly increase the pH of the solution, so more sulfuric acid solution was needed to adjust the pH of the solution. The use of Na_2HPO_4 as a precipi-

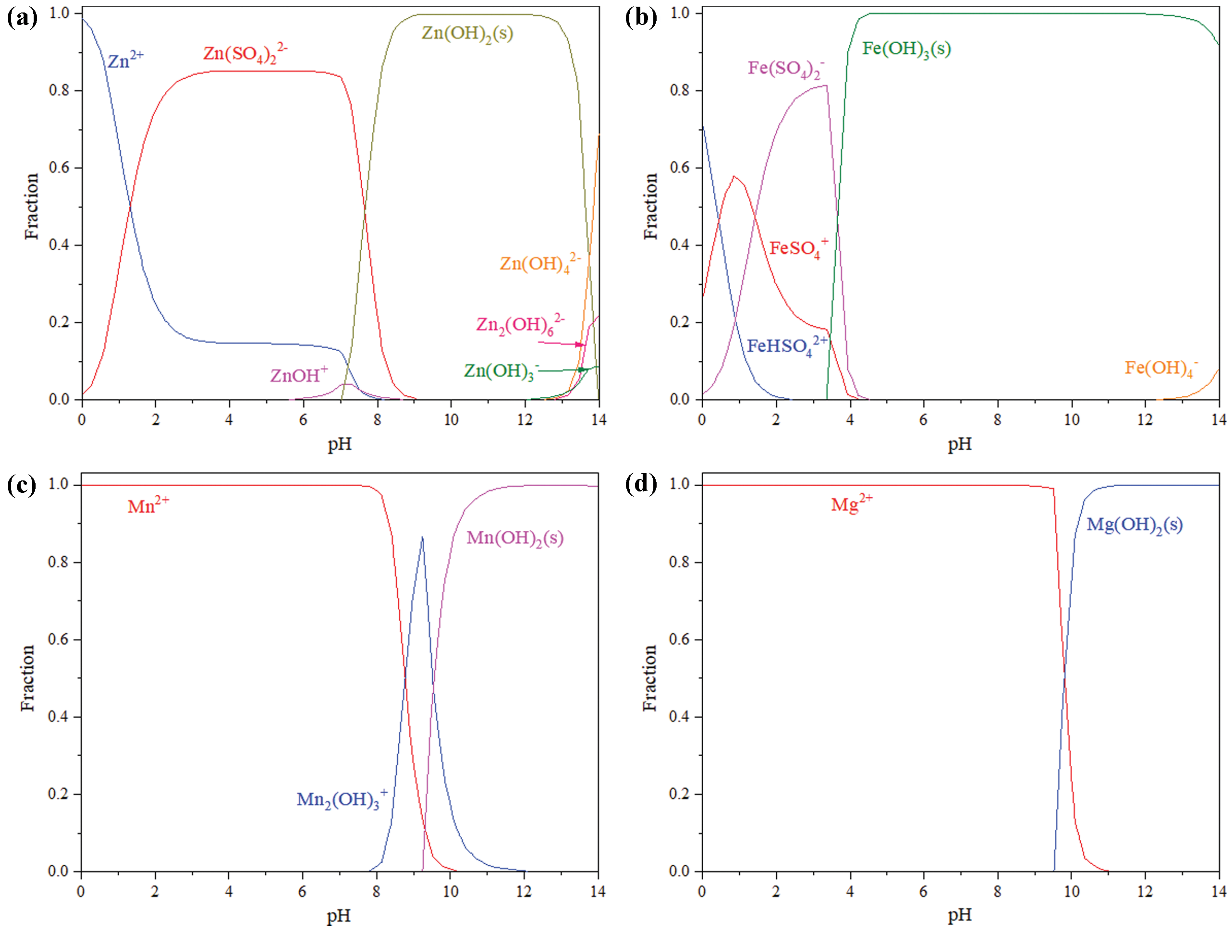

Fig. 1. Species distribution diagrams of Zn-Fe-Mn-Mg-SO_4^{2-} systems containing 5.47 g/L Zn, 2.64 g/L Fe, 1.78 g/L Mn, 0.09 g/L Mg and 24.47 g/L SO_4^{2-}, respectively.

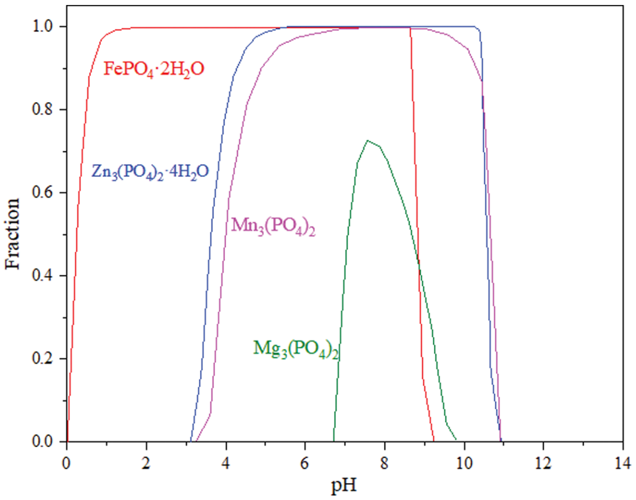

Fig. 2. $FePO_4 \cdot 2H_2O$, $Zn_3(PO_4)_2 \cdot 4H_2O$, $Mn_3(PO_4)_2$, and $Mg_3(PO_4)_2$ distribution curves of Fe-Zn-Mn-Mg-PO_4^{3-} systems containing 2.64 g/L Fe, 5.47 g/L Zn, 1.78 g/L Mn, 0.09 g/L Mg and 9.50 g/L PO_4^{3-}.

tant can avoid this problem. Therefore, in the experiment of iron removal, Na_2HPO_4 was used as precipitant, and the effects of pH of the solution, the dosage of Na_2HPO_4, reaction temperature, and reaction time on the precipitation efficiency of iron and zinc were investigated by single factor experiment. The stirring speed of the whole reaction process was controlled at 400 r/min.

2-1. Effect of Solution pH Value on the Removal of Iron

The pH of the solution not only affects the precipitation efficiency of metals but also affects the separation effect. Fig. 2 shows the distribution of the corresponding phosphate precipitates generated by iron, zinc, manganese, and magnesium with different pH in the solution containing 5.47 g/L Zn, 2.64 g/L Fe, 1.78 g/L Mn, 0.09 g/L Mg and 9.50 g/L PO_4^{3-} (0.1 mol/L PO_4^{3-}). Due to the difference in solubility products of various phosphate precipitates, the solution pH required for the conversion of metals (Fe, Zn, Mn, and Mg) into corresponding phosphate precipitates is different. From Fig. 2, it can be seen that when PO_4^{3-} is introduced into the leaching solution, the pH required for the transformation of iron, zinc, manganese, and magnesium in the solution into corresponding phosphate precipitates will increase in turn. The $FePO_4 \cdot 2H_2O$ precipitates can already be observed at the pH of 0, and with the gradual increase of the pH to 1.8, almost all the iron in the solution is converted into the precipitation of $FePO_4 \cdot 2H_2O$. In addition, it can be noticed from the figure that in order to convert zinc in the solution into $Zn_3(PO_4)_2 \cdot 4H_2O$ precipitates, the pH of the solution requires a value greater than 3.1, and zinc can be precipitated completely only when the pH value is about 5. However, when the pH value is higher than 3.2, $Mn_3(PO_4)_2$ precipitates are formed. The precipitation pH range of $Zn_3(PO_4)_2 \cdot 4H_2O$ and $Mn_3(PO_4)_2$ is very close, so the separation of zinc and manganese in the solution cannot be realized by the phosphate precipitation method. The precipitation of $Mg_3(PO_4)_2$ requires a higher pH value, and the corresponding precipitation can only be formed when the pH is 6.7.

Table 2. Precipitation efficiency of Fe and Zn at different pH

pH	Precipitation efficiency of Fe (%)	Precipitation efficiency of Zn (%)
1.0	83.79	0.09
1.5	92.64	0.12
2.0	97.84	0.15
2.2	99.16	0.21
2.4	99.28	0.58

By adding a certain amount of Na_2HPO_4 to the leaching solution and adjusting the pH of the solution within a certain range, iron can be selectively converted into $FePO_4 \cdot 2H_2O$ precipitates, while zinc continues to exist in the solution, to achieve the purpose of separating iron and zinc. Therefore, the influence of pH on the precipitation efficiency of iron and zinc was explored under the molar ratio of Na_2HPO_4 to Fe of 1.2 : 1, reaction temperature of 30 °C, and reaction time of 60 min. The precipitation efficiency of iron and zinc at different pH is shown in Table 2.

It can be seen from Table 2 that the pH of the solution has a great influence on the precipitation efficiency of iron. When the pH was increased from 1.0 to 2.2, the precipitation efficiency of iron increased from 83.79% to 99.16%, while the precipitation efficiency of zinc increased from 0.09% to 0.21%. However, when the pH of the solution was further increased, the precipitation efficiency of iron remained unchanged, while that of zinc increased to 0.58%. Therefore, to reduce the loss of zinc as much as possible, the optimal precipitation pH was finally determined to be 2.2.

2-2. Effect of Na_2HPO_4 Dosage on Removal of Iron

The influence of Na_2HPO_4 dosage on the precipitation efficiency of iron and zinc was studied at the pH of 2.2, reaction temperature of 30 °C, and reaction time of 60 min. The precipitation efficiency of iron and zinc at different Na_2HPO_4 dosages is shown in Fig. 3.

As shown in Fig. 3, when the molar ratio of Na_2HPO_4 to Fe was 1 : 1, the precipitation efficiency of iron was 94.01% and that of zinc was 0.11%. With the further increase of the dosage of Na_2HPO_4,

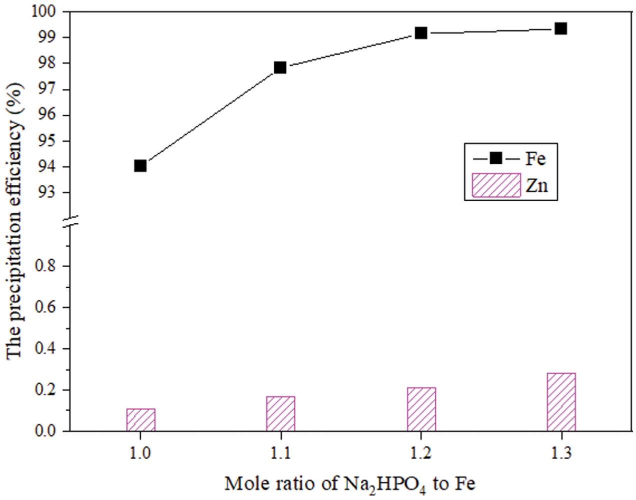

Fig. 3. Influence of Na_2HPO_4 dosage on Fe and Zn precipitation efficiency.

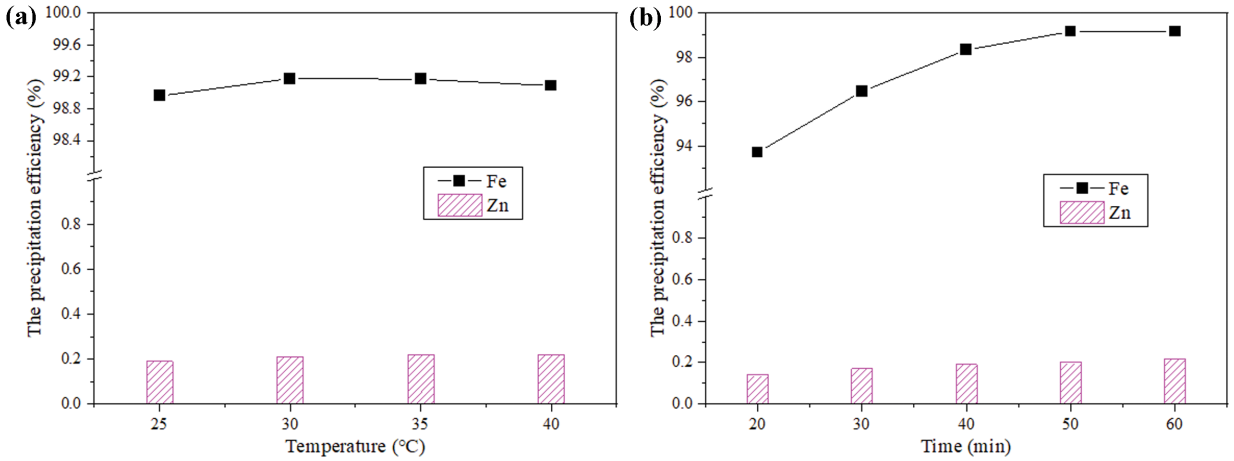

Fig. 4. Influence of reaction temperature (a) and reaction time (b) on Fe and Zn precipitation efficiency.

the precipitation efficiency of iron and zinc increased slowly. When the molar ratio of Na_2HPO_4 to Fe was 1.2 : 1, the precipitation efficiency of zinc increased to 99.16%, which realizes the complete precipitation of iron, and the precipitation efficiency of zinc was only 0.21%. After that, the dosage of Na_2HPO_4 increased again, and the precipitation efficiency of iron remained basically unchanged, which not only increased the dosage of precipitant but also further increased the precipitation efficiency of zinc. Therefore, considered comprehensively, the molar ratio of Na_2HPO_4 to Fe of 1.2 : 1 was determined as the best dosage of Na_2HPO_4.

2-3. Effect of Reaction Temperature and Time on the Removal of Iron

The effects of reaction temperature and time on the precipitation efficiency of iron and zinc were studied under the pH of the solution of 2.2 and the dosage of Na_2HPO_4 1.2 times the molar amount of Fe. The precipitation efficiency of iron and zinc at different reaction temperatures and reaction times is shown in Fig. 4.

Fig. 4(a) reveals the influence of reaction temperature on the precipitation efficiency of iron and zinc under the solution pH of 2.2, the molar ratio of Na_2HPO_4 to Fe of 1.2 : 1, and the reaction time of 60 min. The phenomenon that the reaction temperature has little effect on the precipitation efficiency of iron and zinc can be observed in Fig. 4(a). When the precipitation reaction was carried out at 25 °C, the precipitation efficiency of iron and zinc was 98.96% and 0.19%, respectively. The precipitation efficiency of iron and zinc increased to 99.18% and 0.21% when the reaction temperature was increased to 30 °C. As the reaction temperature continued to increase, the precipitation efficiency of iron decreased slightly, while the precipitation efficiency of zinc remained relatively stable. Hence, it was finally determined that the optimal reaction temperature was 30 °C. Fig. 4(b) demonstrates the effect of reaction time on the precipitation efficiency of iron and zinc under the optimum conditions determined above. With the increase of reaction time from 20 to 50 min, the precipitation efficiency of iron increased from 93.71% to 99.17%, while that of zinc increased from 0.14% to 0.20%. After 50 min, the reaction time continued to be extended, and the precipitation efficiency of iron remained relatively stable. Consequently, the optimal reaction time was determined to be 50 min.

Based on the above analysis, the final optimal conditions for removal of iron were as follows: pH of the solution of 2.2, amount of Na_2HPO_4 1.2 times the molar amount of Fe in the solution, reaction temperature of 30 °C, and reaction time of 50 min. Under these conditions, the precipitation efficiency of iron reached 99.17%, while that of zinc was only 0.20%, which basically realizes the complete removal of iron from the leaching solution.

3. Solvent Extraction of Zn with Cyanex 302 in Kerosene

The filtrate after iron removal mainly contains 5.46 g/L Zn, 1.78 g/L Mn, 0.09 g/L Mn and 0.021 g/L Fe, which is the original solution for extracting zinc with Cyanex 302. The effects of aqueous pH, Cyanex 302 concentration, and phase ratio (O/A) on zinc extraction efficiency were investigated at the extraction temperature of 25 °C and extraction time of 8 min by a single factor experiment.

3-1. Effect of Initial pH on Zinc Extraction Efficiency

Under the conditions of Cyanex 302 concentration of 25%, and phase ratio (O/A) of 2 : 1, the influence of pH of the aqueous phase

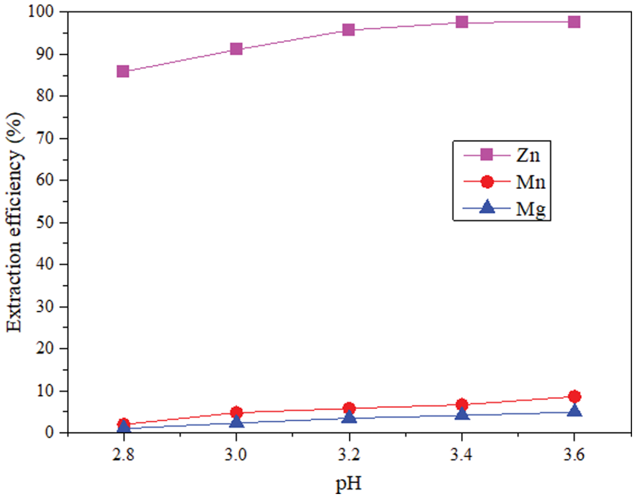

Fig. 5. Effect of aqueous pH on extraction efficiency of zinc.

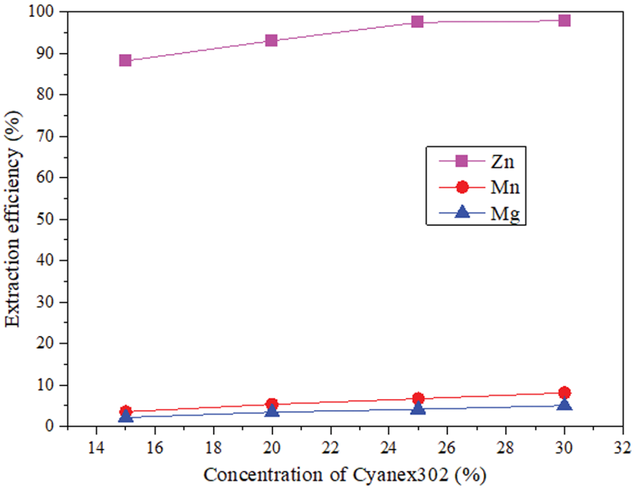

Fig. 6. Effect of Cyanex 302 concentration on extraction efficiency of zinc.

on zinc extraction efficiency was explored, and the results are shown in Fig. 5. As seen in Fig. 5, the pH of the aqueous phase was increased from 2.8 to 3.4, and the extraction efficiency of zinc increased from 85.82% to 97.51%. In this process, the extraction efficiency of manganese rose from 2.05% to 6.71%, while the extraction efficiency of magnesium increased from 1.07% to 4.18%. Nevertheless, the pH of the aqueous phase was further increased to 3.6, the extraction efficiency of zinc remained relatively stable, while the extraction efficiency of manganese and magnesium increased to 8.67% and 4.98%, respectively. Based on the above analysis, it can be seen that when the pH of the aqueous phase was higher than 3.4, it was not conducive to extracting zinc from the sulfuric acid solution containing manganese and magnesium by Cyanex 302 extractant. Consequently, in the follow-up study, 3.4 was selected as the best initial aqueous pH.

3-2. Effect of Cyanex 302 Concentration on Zn Extraction

Fig. 6 shows the effect of Cyanex 302 concentration on zinc extraction efficiency under an aqueous pH of 3.4 and phase ratio (O/A) of 2 : 1. It can be observed from Fig. 6 that the increase in extractant concentration was beneficial to the extraction of zinc. The single-stage extraction efficiency of zinc was 97.50% as the Cyanex 302 concentration of 25%. Co-extraction efficiency of manganese and magnesium reached 6.74% and 4.16% at the Cyanex 302 extractant concentration of 25%, respectively. To further improve the extraction efficiency of zinc, the concentration of Cyanex 302 extractant was increased to 30%. However, the extraction efficiency of zinc was not significantly improved, while the co-extraction efficiency of manganese and magnesium reached 8.14% and 5.05%, respectively. In addition, the viscosity of the organic phase would increase with the increase of extractant concentration, which could make the phase separation effect worse [46]. Therefore, based on the above analysis, to achieve a better separation effect of zinc and impurities, the best concentration of Cyanex 302 extractant was finally selected as 25% (V/V).

3-3. Effect of Phase Ratio (O/A) on Zn Extraction

Under the conditions of pH 3.4, Cyanex 302 concentration of 25%, extraction time of 8 min, and extraction temperature of 25 °C, the influence of phase ratio (O/A) on extraction efficiency of zinc was researched, and the detailed experimental results are shown in Fig. 7(a). When the phase ratio was 0.5 : 1, the extraction efficiency of zinc was only 78.29%, while the extraction efficiency of zinc rapidly increased to 97.52% when the phase ratio was increased to 2 : 1. In the process of increasing the phase ratio from 0.5 to 2.0, the co-extraction efficiency of manganese and magnesium increased from 2.78% and 1.74% to 6.71% and 4.17%, respectively. However, when the phase ratio was further increased to 2.5, not only was the extraction efficiency of zinc not improved, but also the co-extraction efficiency of manganese and magnesium was significantly increased. The increase in the phase ratio will not only lead to an increase in extractant consumption but also cause trouble for the stripping process. Based on this, it was finally determined that the volume ratio of the organic phase to the aqueous phase was 2 : 1.

Through the above single-factor extraction experiments, it can be seen that at the above optimum conditions, the one-stage extraction efficiency of zinc was 97.52%, and 2.48% of zinc remained in the aqueous phase. Therefore, the McCabe-Thiele equilibrium isotherm should be established to determine the extraction stages

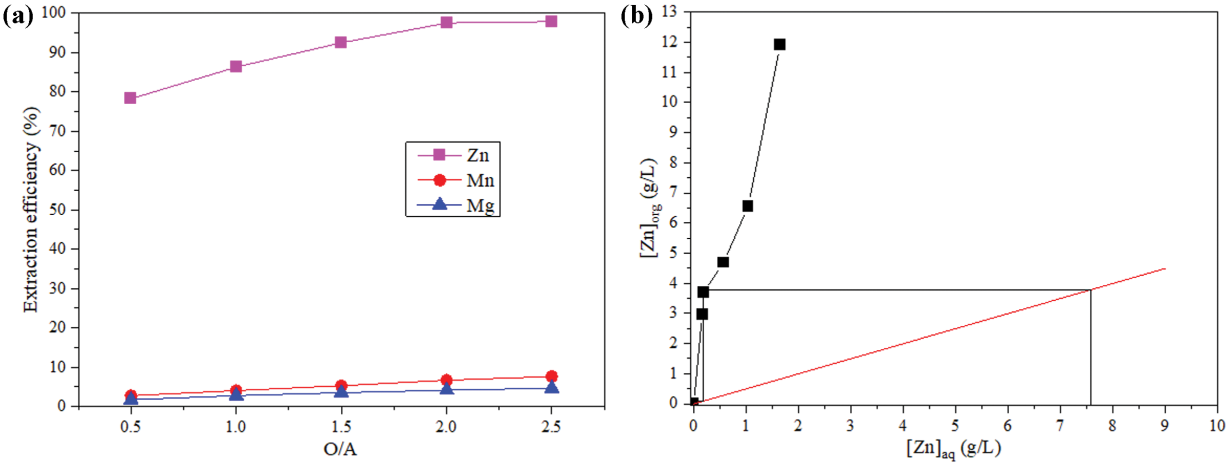

Fig. 7. (a) Effect of phase ratio (O/A) on zinc extraction efficiency; (b) McCabe-Thiele plot for zinc extraction.

Table 3. The extraction efficiency of metals by two-stage countercurrent extraction

Items	Zn	Mn	Mg	$\beta_{Zn/Mn}$
C_0 (g/L)	5.46	1.78	0.09	33987.78
C_{aq} (g/L)	0.003	1.69	0.087	
C_{org} (g/L)	2.715	0.045	0.0013	
E (%)	99.94	5.05	2.87	

of completely extracting zinc. Under the condition of 25% Cyanex 302 extractant concentration, the McCabe-Thiele equilibrium isotherm was determined by changing the phase ratio as shown in Fig. 7(b). The results of Fig. 7(b) indicate that, theoretically, zinc in the solution could be completely extracted by two-stage countercurrent extraction. For verifying the predicted results of the McCabe-Thiele equilibrium isotherm, a two-stage countercurrent experimental process was conducted under the above-mentioned optimal experimental conditions (aqueous pH of 3.4, Cyanex 302 concentration of 25%, O/A of 2 : 1, extraction temperature of 25 °C and extraction time of 8 min). The experimental outcomes are presented in Table 3.

As observed from Table 3 above, after two-stage countercurrent extraction, the zinc concentration in the solution decreased from 5.46 g/L to 0.003 g/L, and the extraction efficiency of zinc was 99.94%. Through two-stage countercurrent extraction, the concentration of zinc in the organic phase was 2.715 g/L, while the concentrations of manganese and magnesium were only 0.045 g/L, and 0.0013 g/L, respectively. The separation factor (β) of Zn/Mn was as high as 33,987.78, indicating that Cyanex 302 extractant can extract zinc selectively from solutions containing manganese very well. The experimental data in Table 3 demonstrates that the zinc in the solution could be completely extracted through two-stage countercurrent extraction, and the extraction efficiency was over 99.9%, which confirmed the predicted results in Fig. 7(b).

4. Thermodynamic Analysis of Zn Extraction with Cyanex 302

The reaction formula for extraction of zinc from sulfuric acid solution by Cyanex 302 extractant is as follows:

$$Zn^{2+}+3HA_{org}=ZnA_2(HA)_{org}+2H^+ \tag{6}$$

where HA_{org} denotes the Cyanex 302.

At a certain temperature, the extraction equilibrium constant (K_{ex}) and extraction partition coefficient (D) in the process of extracting zinc by Cyanex 302 can be calculated by the following equation:

$$K_{ex}=\frac{[ZnA_2(HA)_{org}]\times[H^+]^2}{[Zn^{2+}]\times[HA]^3} \tag{7}$$

$$D=\frac{[ZnA_2(HA)]_{org}}{[Zn^{2+}]_{aq}} \tag{8}$$

$$D=\frac{K_{ex}\times[HA]^3}{[H^+]^2} \tag{9}$$

Eq. (10) can be obtained based on the above Eqs. (7) to (9).

$$lgD=lgK_{ex}+3lg[HA]-2lg[H^+] \tag{10}$$

Eq. (11) can be obtained from the van't Hoff equation:

Table 4. Effect of temperature on extraction efficiency and partition coefficient of zinc

T (K)	298.15	308.15	318.15	328.15	338.15
E (%)	99.17	98.91	98.67	98.34	97.95
D	59.741	45.372	37.094	29.620	23.890

$$lgD=-\frac{\Delta H}{2.303RT}+C \tag{11}$$

where R, T, and C are the gas constant, absolute temperature, and integral constant, respectively.

Experiments with different extraction temperatures were carried out under the initial aqueous pH of 3.4, Cyanex 302 concentration of 25%, phase ratio (O/A) of 2 : 1, and extraction time of 8 min. The extraction efficiency and extraction partition coefficient of zinc at different extraction temperatures are shown in Table 4.

From Table 4, it can be clearly observed that with the increase in extraction temperature, the extraction efficiency and extraction partition coefficient of zinc decreased continuously. When the extraction temperature increased from 298.15 K to 338.15 K, the extraction efficiency and extraction partition coefficient of zinc decreased from 99.17% and 59.741 to 97.95% and 23.890, respectively.

According to the experimental results in Table 4, the linear regression equation (lgD-1000/T) was obtained, and the results are presented in Fig. 8. As seen from Fig. 8, the curve has a very good fitting degree, with a linear correlation coefficient of 0.9987 (R^2) and equation slope (k) of 0.9889. The enthalpy changes of zinc extraction by Cyanex 302 extractant at a certain temperature can be calculated as follows by Eq. (12):

$$\Delta H=-2.303Rk \tag{12}$$

where R (gas constant) is 8.314 kJ/mol, and k is the slope of the fitting equation.

The results show that the enthalpy changes of the zinc extraction process with Cyanex 302 extractant were −18.935 kJ/mol ($\Delta H<0$), indicating that the extraction process with Cyanex 302 of zinc is

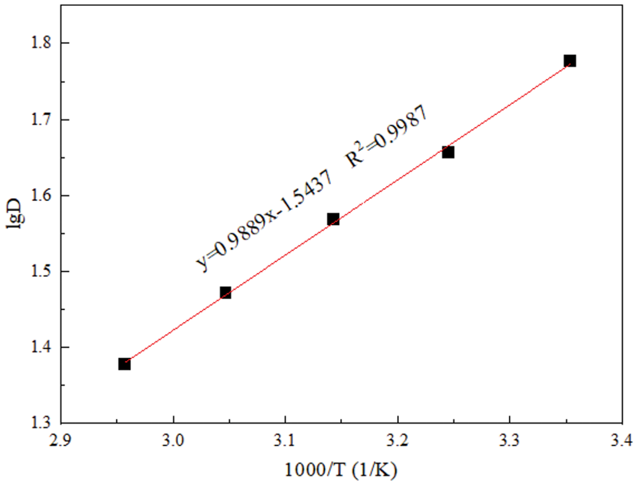

Fig. 8. Linear result of lgD versus 1,000/T for zinc extraction using Cyanex 302.

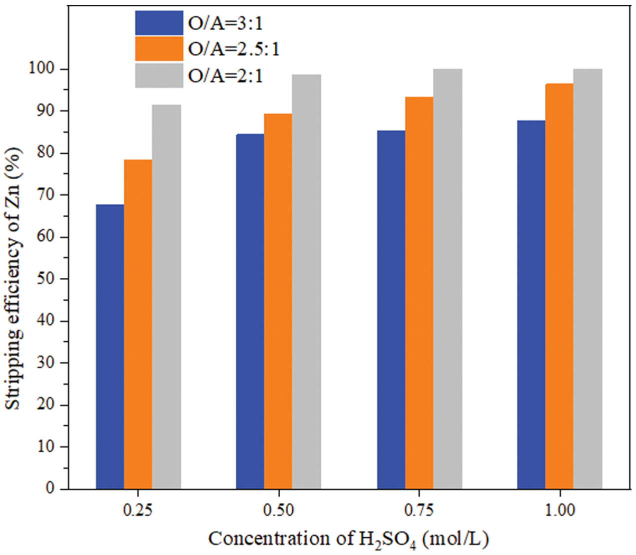

Fig. 9. Effect of sulfuric acid concentration and phase ratio (O/A) on zinc stripping efficiency.

an exothermic reaction, so low temperature is more conducive to the extraction of zinc by Cyanex 302.

5. Stripping Zn from the Organic Phase

When extracting zinc with Cyanex 302 extractant, dilute sulfuric acid solution can be used as a stripping agent to strip zinc from the loaded organic phase. To determine the best conditions, under the conditions of stripping time of 10 min and stripping temperature of 25 °C, the effects of different sulfuric acid concentrations and phase ratio (O/A) on zinc stripping efficiency were investigated. The experimental results under different sulfuric acid concentrations and different phase ratios (O/A) are shown in Fig. 9.

As shown in Fig. 9, both sulfuric acid concentration and phase ratio (O/A) have a great influence on the stripping efficiency of zinc. When the O/A was selected as 3 : 1, the concentration of sulfuric acid increased from 0.25 mol/L to 1 mol/L, and the stripping efficiency of zinc increased from 67.51% to 87.73%. After 0.5 mol/L, the stripping efficiency of zinc increased slowly with the increase of sulfuric acid concentration. It can be observed that when the O/A was 3 : 1, the high stripping efficiency of zinc required a high sulfuric acid concentration. When the O/A was reduced to 2.5 : 1, although the sulfuric acid concentration was increased from 0.25 mol/L to 1 mol/L, the stripping efficiency of zinc was improved from 78.24% to 96.32%, but there was still 3.68% zinc in the organic phase. However, it is gratifying to note that the single-stage stripping efficiency of zinc reached 99.96% at the sulfuric acid concentration of 0.75 mol/L when the O/A was reduced to 2 : 1, which indicates that the complete dissolution of zinc in the organic phase has been basically realized.

The barren organic phase was stripped to remove a small number of impurities such as zinc, iron, and magnesium with 1.0 mol/L NaOH solution at an O/A of 1 : 1 and an oscillation time of 5 min, then the alkalized organic phase was regenerated with 1.0 mol/L H_2SO_4 solution at an O/A of 1 : 1 and an oscillation time of 5 min. Then, the recycled organic phase could then be reused again, which greatly reduced the costs of production.

6. Technological Scheme for Recovery of Zn and Fe from Blast-furnace Dust

The process of separating and recovering zinc and iron from blast-furnace dust by ammonium sulfate roasting, water leaching, and solvent extraction was determined, and the specific process parameters are shown in Fig. 10.

1) The blast-furnace dust was roasted at the mass ratio of ammonium sulfate-to-blast-furnace dust of 8 : 5, roasting tem-

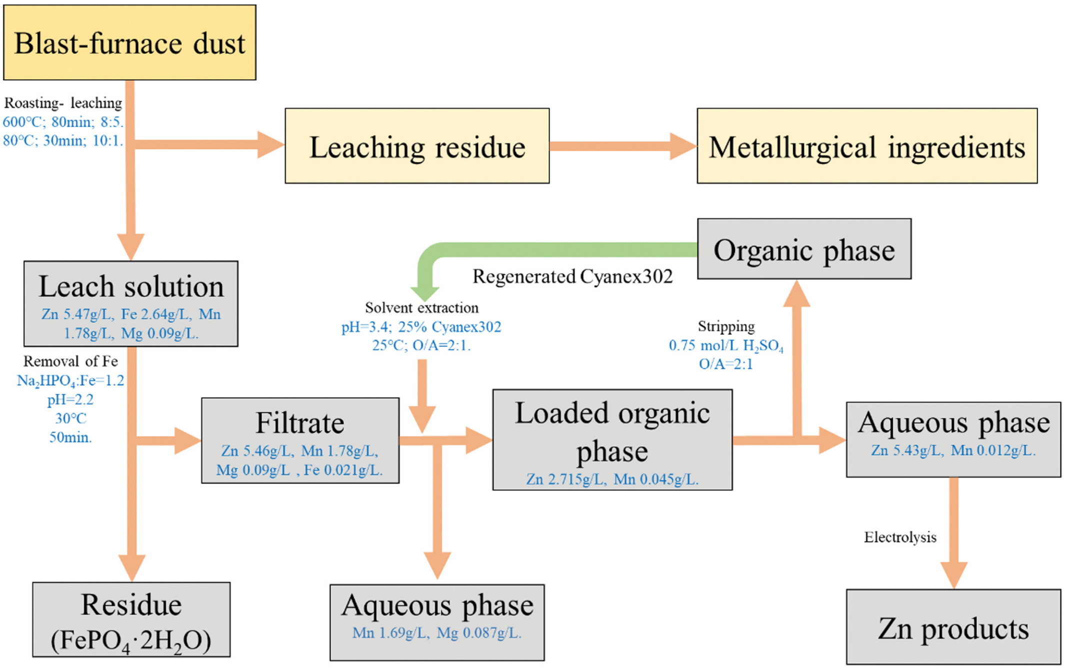

Fig. 10. Process flowsheet for the recovery of Zn and Fe from blast-furnace dust.

perature of 650 °C, and roasting time of 80 min. Then, the roasting slag was leached with pure water under the leaching temperature of 80 °C, mass ratio liquid-solid of 10 : 1, and leaching time of 30 min. Finally, the leaching efficiency of zinc reached 93.64%, while that of iron was only 6.87%. The leached slag mainly consists of iron oxide, which could be used as metallurgical ingredients.

2) Iron in the leaching solution was selectively converted into $FePO_4 \cdot 2H_2O$ precipitate by using Na_2HPO_4 as precipitant. The precipitation efficiency of iron reached 99.17%, while that of zinc was only 0.20% under the solution pH of 2.2, molar ratio of Na_2HPO_4 to Fe of 1.2 : 1, reaction temperature of 30 °C, and reaction time of 50 min, which basically realizes the complete removal of iron from leaching solution.
3) Zinc in the filtrate after iron removal can be well extracted by Cyanex 302 extractant. The extraction efficiency of zinc reached 99.94% through two-stage countercurrent extraction under an initial pH value of 3.4, Cyanex 302 concentration of 25%, and phase ratio (O/A) of 2 : 1, while the organic phase containing 2.715 g/L was obtained. Selective extraction of zinc from the solution mainly containing manganese impurities was realized.
4) At the sulfuric acid concentration of 0.75 mol/L, phase ratio (O/A) of 2 : 1, stripping time of 10 min, and stripping temperature of 25 °C, the single-stage stripping efficiency of zinc reached 99.96%, which shows that the complete stripping of zinc was basically achieved. The stripping solution contained 5.43 g/L zinc, which could be used to obtain zinc products by electrolysis.

CONCLUSIONS

This study investigated the effective separation of Zn, Fe, and Mn from ammonium sulfate roasting-water leaching solution of blast-furnace dust by precipitation and solvent extraction, and the main conclusions are as follows:

(1) The precipitation efficiency of iron reached 99.17%, while that of zinc was only 0.20% under the solution pH of 2.2, molar ratio of Na_2HPO_4 to Fe of 1.2 : 1, reaction temperature of 30 °C, and reaction time of 50 min. The filtrate after removal of iron by precipitation with Na_2HPO_4 mainly contains 5.46 g/L Zn, 1.78 g/L Mn, and 0.09 g/L Mn, which is the original solution for extracting zinc with Cyanex 302.

(2) The Cyanex 302 extractant can selectively extract zinc from a sulfuric acid solution containing manganese. The Zn (99.94%) could be extracted through two-stage countercurrent extraction under an initial pH value of 3.4, Cyanex 302 concentration of 25%, and phase ratio (O/A) of 2 : 1. In addition, the extraction of Zn from sulfuric acid solution with Cyanex 302 is an exothermic reaction by thermodynamic calculations.

(3) The single-stage stripping efficiency of zinc reached 99.96% at the sulfuric acid concentration of 0.75 mol/L, phase ratio (O/A) of 2 : 1, stripping time of 10 min, and stripping temperature of 25 °C. A stripping solution with 5.43 g/L Zn could be used to obtain zinc products by electrolysis. The proposed process flowsheet may be used to efficiently recover Zn and Fe from blast-furnace dust.

ACKNOWLEDGEMENTS

This research was supported by China Ocean Mineral Resources R&D Association under Grant No. JS-KTHT-2019-01.

DECLARATION OF INTEREST STATEMENT

This article has not been published elsewhere in whole or in part. All authors have read and approved the content and agree to submit it for consideration for publication in the journal. There are no ethical/legal conflicts involved in the article. If accepted, the article will not be published elsewhere in the same form, in any language, without the written authorization of the Publisher.

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