Centrifugal extraction of rare earths from wet-process phosphoric acid

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Abstract

Phosphorite ore is a potential resource of rare earths (RE) as well as phosphate; therefore, the recovery of RE from wet-process phosphoric acid (WPA) is promising. This study investigated the influence of rotational speed, extractant concentration, flow ratio and phase contact time on the centrifugal extraction of RE from WPA and the separation of RE from impurities. The results indicate that higher rotational speed, higher extractant concentration and larger flow ratio are beneficial to the extraction of RE and impurities from phosphoric acid. It is found that the phase contact time for efficiently extracting RE and that for iron are of great difference, which provides an effective method for separating RE from iron using the non-equilibrium extraction process in centrifugal contactors. Compared with equilibrium extraction, the separation factor $\beta_{RE/Fe}$ is enhanced from 0.07 to 17.6.

Keywords: hydrometallurgy; centrifugal extraction; rare earths; phosphoric acid

1. Introduction

Phosphorite is a rare earths (RE)-bearing mine [1] (average 0.5 wt.‰ RE [2]). The total reserve of phosphorite ore in the world is about 100 billion tons [3-4]. Hence, various recovery techniques of RE from phosphorite have been developed [2, 5-7]. Wet processing, using the digestion of phosphate rocks by sulfuric acid, is the most widely used process to produce phosphoric acid. In wet process, RE are usually enriched in phosphoric acid [2]. Therefore, it is necessary to study the recovery of RE from wet-process phosphoric acid (WPA).

Compared with mixer-settlers widely applied in the hydrometallurgical industry of RE, a centrifugal contactor has several advantages, such as low holdup volume, excellent phase separation, high mass transfer efficiency, short startup time, compact and short pieces of equipment, etc. In addition, it has been successfully applied in some fields, including hydrometallurgy, wastewater treatment, biotechnology and pharmaceutical industry [8-9].

Generally, WPA contains some other impurities, such as Fe^{3+}, Al^{3+}, Ca^{2+} and Mg^{2+}. It is found that without reducing Fe^{3+} to Fe^{2+}, the separation of RE from iron in phosphoric acid with di(2-ethylhexyl) phosphoric acid (D2EHPA) during the equilibrium extraction process is difficult due to their similar and high distribution coefficients [2]. However, it is also found that the mass transfer velocities of RE and iron during the extraction process are of great difference, indicating that they can be separated in a non-equilibrium extraction manner despite their similar distribution coefficients. The operation of non-equilibrium extraction requires a suitable contactor to enable two phases to mix quickly and thoroughly and then settle immediately. Also, the phase contact time must be short enough so that species with a large mass transfer velocity can be extracted, while the other components with a low mass transfer velocity cannot be extracted due to deviation from thermodynamic equilibria. Among available contactors, only the centrifugal contactor satisfies the requirements [8, 10]. Hence, this study focuses on the centrifugal extraction of RE from WPA and the separation between RE and impurities.

2. Experimental

Generally, after the purification of WPA by solvent extraction, the content of P_2O_5 in raffinate varies from 5 wt.% to 10 wt.% [4, 11]. Hence, the concentration of phosphoric acid was chosen as 10 wt.% P_2O_5 for further centrifugal extraction studies. Phosphoric acid used in this study consists of 1.0 g/L REO, 0.3 g/L Fe_2O_3, 0.3 g/L Al_2O_3, 0.8 g/L MgO and 0.8 g/L CaO, as shown in Table 1. D2EHPA was diluted with kerosene to the required concentration. Kerosene was

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					Table 1. Contents of some metal elements in WPA						mg/L
La_2O_3	CeO_2	Pr_5O_{11}	Nd_2O_3	Sm_2O_3	Gd_2O_3	Dy_2O_3	Y_2O_3	Fe_2O_3	Al_2O_3	MgO	CaO
199.4	426.5	56.3	232.9	55.0	28.9	17.1	27.9	290.3	313.5	780.5	813.7

sulfonated before use. Stock solutions of each RE were prepared by dissolving their oxide with a purity of 99.9% in concentrated sulfuric acid and diluting with deionized water. All reagents were reagent-grade unless indicated. Centrifugal extraction was carried out in an HL-20 centrifugal contactor made by Beijing Institute of Applied Technology of Extraction. After stable operation, aliquot of aqueous solution was taken to analyze RE and other metal ions using inductively coupled plasma (ICP) [12].

3. Results and discussion

3.1. Effect of rotational speed on extraction degree of metal ions

Figs. 1 and 2 show the influence of rotational speed on the extraction degree (E) of metal ions and RE, respectively. The extraction degree of iron increases sharply from 15.6% when the rotational speed is 2500 r/min to 63.1% when the rotational speed reaches 4000 r/min. Beyond 4000 r/min, the rotational speed has less effect on the iron extraction, while extraction degree of Ca^{2+}, Mg^{2+}, Al^{3+} and RE remains almost unaltered. Thus, a decrease in rotational speed could enhance the separation of RE from iron. When the flow ratio and the contact time remain constant, the increase in rotational speed results in a better mixing of the two phases. Therefore, the extraction degree of iron increases due to its low mass transfer velocity and the interfacial chemical reaction having a predominant effect on determining the extraction [13]. However, the extraction degree of RE and other impurities remains constant due to their very high mass transfer velocity.
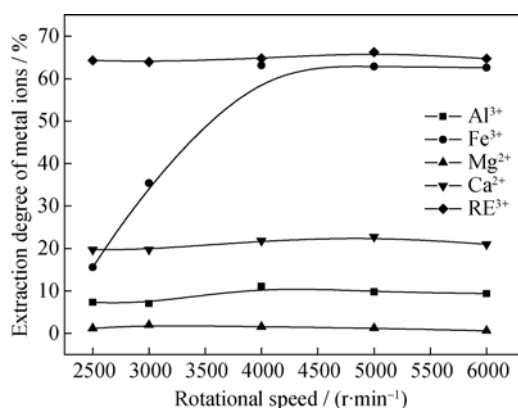
Fig. 2. Effect of rotational speed on the extraction of RE (298 K, phosphoric acid with 10 wt.% P_2O_5 and 1 g/L REO, 1.5 mol/L D2EHPA, O/W = 2, with a flow of 60 mL/min).

3.2. Effect of D2EHPA concentration on extraction degree of metal ions

In general, the distribution coefficient (D) increases with increasing extractant concentration, and it is preferable to have high extractant concentration for a better extraction of RE. However, high concentration of D2EHPA increases the viscosity of the organic phase and therefore decreases the mass transfer coefficient.

The extraction degree of RE increases as a function of D2EHPA concentration and reaches 71.3% with 2.0 M D2EHPA (Fig. 3). It can be seen that the extraction efficiency for the elements by D2EHPA is in the order La<Ce<Pr<Nd<Sm<Gd<Dy<Y, which increases with increasing atomic number (except for Y) and is consistent with the results reported by Wang *et al.* [2]. However, high

Fig. 1. Effect of rotational speed on the extraction of metal ions (298 K, phosphoric acid with 10 wt.% P_2O_5 and 1 g/L REO, 1.5 mol/L D2EHPA, flow ratio O/W = 2, with a flow of 60 mL/min).
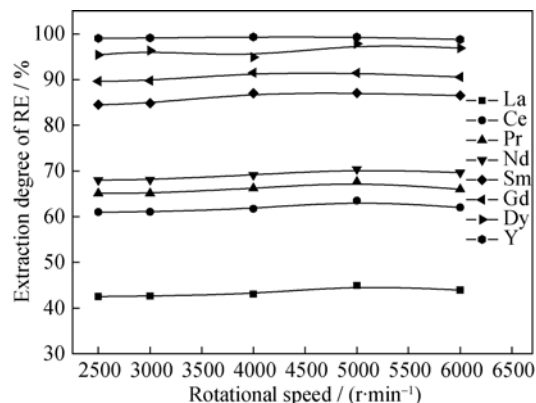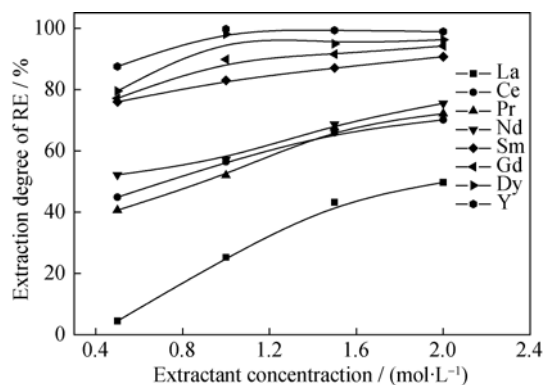
Fig. 3. Effect of D2EHPA concentration on the extraction of RE (298 K, phosphoric acid with 10 wt.% P_2O_5 and 1 g/L REO, O/W = 2, 3000 r/min rotational speed, with a flow of 60 mL/min).

extractant concentrations also favor extraction of other metal ions (as shown in Fig. 4), which deteriorates the separation between lanthanides and other metal ions.
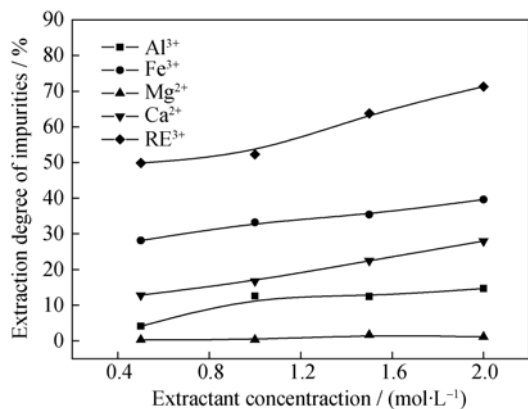

Fig. 4. Effect of D2EHPA concentration on the extraction of metal ions (298 K, phosphoric acid with 10 wt.% P_2O_5 and 1 g/L REO, O/W = 2, 3000 r/min rotational speed, with a flow of 60 mL/min).

3.3. Effect of flow ratio O/W on extraction degree of metal ions

The flow ratio O/W was varied between 1/3 and 3/1 under the following operating conditions: [D2EHPA] = 1.5 mol/L, phosphoric acid with 10 wt.% P_2O_5 and 1 g/L REO at 298 K. Results are shown in Figs. 5 and 6. Increasing the flow ratio O/W from 1/3 to 1/1 leads to an increase in the extraction degree of RE^{3+} from 18.5% to 60.8%, Fe^{3+} from 14.9% to 33.8%, Ca^{2+} from 2.4% to 19.7% and Al^{3+} from 3.3% to 11.1%, while that of Mg^{2+} remains almost constant. The light RE are difficult to be extracted at low flow ratio O/W. In addition, the effect of increase on extraction degree of light RE is more obvious. However, beyond 1/1, the flow ratio has less effect.
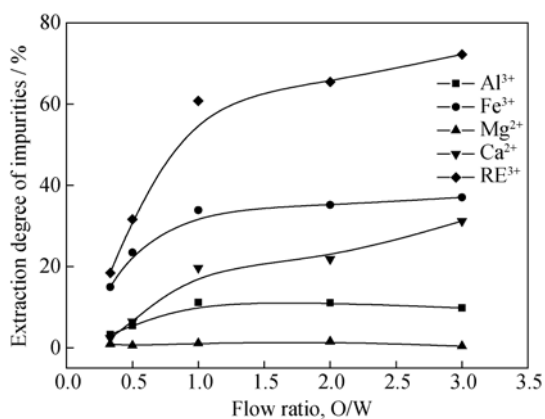

Fig. 5. Effect of flow ratio on the extraction of metal ions (298 K, phosphoric acid with 10 wt.% P_2O_5 and 1 g/L REO, 1.5 mol/L D2EHPA, 3000 r/min rotational speed, with a flow of 60 mL/min).
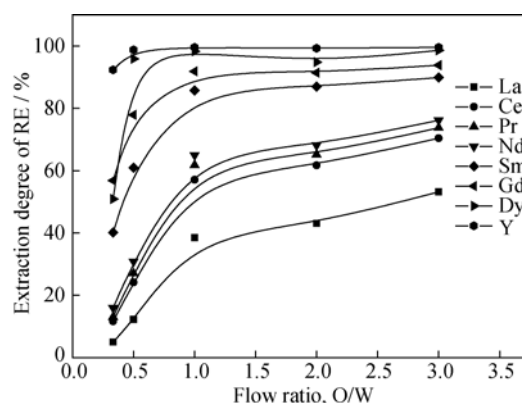

Fig. 6. Effect of flow ratio on the extraction of RE (298 K, phosphoric acid with 10 wt.% P_2O_5 and 1 g/L REO, 1.5 mol/L D2EHPA, 3000 r/min rotational speed, with a flow of 60 mL/min).

3.4. Effect of phase contact time on extraction degree of metal ions

Due to high distribution coefficients of RE^{3+} and Fe^{3+}, it is hard to separate RE from iron in phosphoric acid with D2EHPA during equilibrium extraction process [2]. Provided that the difference of the mass transfer velocity between two components is large enough, they could be separated in non-equilibrium extraction despite the same distribution coefficient. Therefore, special attention was paid to the effect of phase contact time on the extraction of RE and impurities.

The phase contact time (*T*) in the centrifugal contactor was calculated by the equation:

$T = 60VQ^{-1}$,

where *Q* (mL/min) is the total flow rate and *V* (mL) represents the mixed volume of two phases. Therefore, the phase contact time can be controlled by the total flow rate.

A series of experiments were then performed at phase contact time ranging from 8 to 20 s at 298 K, with rotational speed 3000 r/min and O/W = 2. Results in Fig. 7 indicate that the mass transfer velocity of RE is much faster than that of iron, when the phase contact time is very short in the contactor, RE can be well separated from iron in the non-equilibrium extraction process with centrifugal contactors. Thus, the contact time between two phases must be short enough so that RE with a large mass transfer velocity can be extracted into the organic solvent according to its distribution coefficient, while Fe^{3+} with a low mass transfer velocity cannot be extracted due to deviation from thermodynamic equilibrium.

Both the distribution coefficients and the separation factors were important for separation of RE from impurities, so the separation factors of RE and impurities under optimum conditions must be determined, as shown in Table 2. The dis-
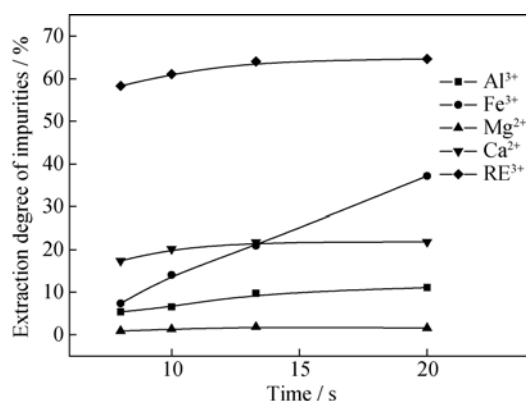
Fig. 7.   Effect of phase contact time on the extraction of metal ions (298 K, phosphoric acid with 10 wt.% P_2O_5 and 1 g/L REO, 1.5 mol/L D2EHPA, O/W = 2, 3000 r/min rotational speed).

Table 2.   Parameters of metal ions under optimum condition

Ions	RE^{3+}	Fe^{3+}	Al^{3+}	Mg^{2+}	Ca^{2+}
E / %	58.5	7.2	5.3	0.9	15.7
D / (mol·L^{-1})	1.41	0.08	0.06	0.01	0.19
β	—	17.6	23.5	141	7.4
β_{eq}	—	0.07	12.7	104	6.8

Note: Optimum conditions—298 K, phosphoric acid with 10 wt.% P_2O_5 and 1 g/L REO, 1.5 mol/L D2EHPA, O/W = 1, 3000 r/min rotational speed, and contact time of 8 s; β—the separation factor of RE and other metal ions; β_{eq}—the equilibrium separation factor.

tribution coefficient was calculated by the following equation:

$$D = [RE]_{o,eq}/[RE]_{w,eq,}$$

where $[RE]_{o,eq}$ and $[RE]_{w,eq}$ are the equilibrium concentrations of RE ion in organic phase and aqueous phase, respectively (mol/L).

The separation factor was calculated by the following equation [9]:

$$\beta = D_1/D_2,$$

where β is the separation factor of two kinds of ions, and D_1 and D_2 are the distribution coefficients of two kinds of ions in the same system.

The results in Table 2 show that all the separation factors of RE and impurities exceed 7, and the RE can be well separated from the impurities with centrifugal contactors. Particularly, $\beta_{RE/Fe}$ is enhanced from 0.07 to 17.6 compared to equilibrium extraction. In addition, in this paper, it can be found that the extraction degree of aluminum from phosphoric acid is very low, compared to hydrochloric acid, nitric acid and sulfuric acid systems, which is consistent with the results reported by Wang *et al.* [2] and El-Khaiary [14]. Yu *et al.* [15-16] found that the extraction of aluminum from

phosphoric acid with D2EHPA was controlled by the chemical reaction inner the micellization, thus the extraction mechanism is yet to be deeply developed.

4. Conclusions

The research on the centrifugal extraction technique of RE from WPA leads to the following conclusions:

(1) RE can be extracted efficiently by D2EHPA, and the extraction efficiency for the elements follows the order La<Ce<Pr<Nd<Sm<Gd<Dy<Y, which increases with increasing atomic number (except for Y).

(2) Due to the high distribution coefficients of RE and Fe^{3+}, it is hard to separate RE from iron in phosphoric acid with D2EHPA during the equilibrium extraction process.

(3) The mass transfer velocity of RE is much faster than that of iron, and when the phase contact time is very short in the contactor, RE can be well separated from iron in the non-equilibrium extraction process with centrifugal contactors.

(4) Compared with equilibrium extraction, the separation factor $\beta_{RE/Fe}$ is enhanced from 0.07 to 17.6 under the optimum conditions: 1.5 mol/L D2EHPA, O/W = 1, 3000 r/min rotational speed and contact time of 8 s.

Acknowledgements

References

[1]   Jorjani E., Bagherieh A.H., Mesroghli Sh., and Chehreh Chelgani S., Prediction of yttrium, lanthanum, cerium, and neodymium leaching recovery from apatite concentrate using artificial neural networks, *J. Univ. Sci. Technol. Beijing*, 2008, **15** (4): 367.

[2]   Wang L.S., Long Z.Q., Huang X.W., Yu Y., Cui D.L., and Zhang G.C., Recovery of rare earths from wet-process phosphoric acid, *Hydrometallurgy*, 2010, **101** (1-2): 41.

[3]   Ilyin A.V., Phosphorites of the Russian Craton, *Earth Sci. Rev.*, 1998, **45** (1-2): 89.

[4]   Becker P., *Phosphates and Phosphoric Acid: Raw Materials, Technology, and Economics of the Wet Process*, Marcel Dekker Inc., New York, 1983.

[5]   Aly M.M. and Mohammed N.A., Recovery of lanthanides from Abu Tartur phosphate rock, Egypt, *Hydrometallurgy*, 1999, **52**: 199.

[6]   Koopman C. and Witkamp G.J., Extraction of lanthanides

from the phosphoric acid production process to gain a purified gypsum and a valuable lanthanide by-product, *Hydrometallurgy*, 2000, **58**: 51.

[7] Long Z.Q., Wang L.S., Huang X.W., Peng X.L., Han Y.B., and Cui D.L., Progress in extraction technique for trace rare earths from phosphorite, *Chin. J. Rare Met.*, 2009, **33** (3): 434.

[8] Leonard R.A., Recent advances in centrifugal contactor design, *Sep. Sci. Technol.*, 1988, **23** (12-13): 1473.

[9] Zhou J.Z., Duan W.H., Zhou X.Z., and Zhang C.Q., Application of annular centrifugal contactors in the extraction flowsheet for producing high purity yttrium, *Hydrometallurgy*, 2007, **85**: 154.

[10] Zhou X.Z., Zhou J.Z., Zhang C.Q., and Yu W.D., Application of annular centrifugal contactor on separating indium from iron, *Sep. Sci. Technol.*, 1997, **32**: 2705.

[11] Hannachi A., Habaili D., Chtara C., and Ratel A., Purification of wet process phosphoric acid by solvent extraction with TBP and MIBK mixtures, *Sep. Purif. Technol.*, 2007, **55**: 212.

[12] Li M.L., Wang L.S., Peng X.L., Yang G.L., Huang X.W., and Long Z.Q., Determination of trace rare earth elements in phosphate ore by inductively coupled plasma atomic emission spectrometry, *Metall. Anal.*, 2010, **31** (1): 47.

[13] Gao Z.L., Sun S.X., Shen J.L., and Yu W.P., Studies on the extraction kinetic of Fe(III) with 2-ethyl hexyl 2-ethyl hexyl phosphoric acid (HEH[EHP]), *Chem. J. Chin. Univ.*, 1988, **11**: 1136.

[14] El-Khaiary M.I., Extraction of Al(III) from phosphoric acid by HDDNSA, *Sep. Purif. Technol.*, 1997, **12**: 13.

[15] Yu J.F. and Xiong Y.G., Kinetics, interfacial chemistry and extraction mechanism of individual extraction system: (I) Interfacial chemistry and extraction mechanism of organo-phosphoric acid extraction system, *Uranium Min. Metall.*, 1993, **12** (1): 26.

[16] Yu J.F., Kinetics, interfacial chemistry and extraction mechanism: (II) Extraction kinetics for micelle extraction system, *Uranium Min. Metall.*, 1993, **12** (2): 93.