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Journal of Alloys and Compounds 408–412 (2006) 995–998

Journal of ALLOYS AND COMPOUNDS

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A new hydrometallurgical process for extracting rare earths from apatite using solvent extraction with P_{350}

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Received 29 July 2004; received in revised form 22 November 2004; accepted 2 December 2004
Available online 4 June 2005

Abstract

In this paper, a new process is proposed to recover rare earths from nitric acid leaching of apatite without interfering with the normal route for fertilizer production using solvent extraction with dimethyl heptyl methyl phosphonate $CH_3P(O)(OC_8H_{17})_2$ (P_{350}, B). In the present work, the leaching conditions are studied. In selected condition, apatite was dissolved in 20% (v/v) nitric acid solution at 60–70 °C while agitating. The most suitable acidity for extraction is 0.4 M HNO_3. More than 98% of rare earths in apatite can be recovered using countercurrent extraction process with six stages when phase ratio = 0.5, and defluorination is unnecessary. The influences of phase ratio, stage number, acidity and salting-out agent on extractabilities of P_{350} are studied. The results show that rare earths can be separated with P_{350} from Ca, P, Fe and other impurities. Mixed rare earth oxides (REO) of which purity is more than 95% with yield over 98% can be obtained.

Keywords: Solvent extraction; Rare earths; P_{350}; Apatite

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1. Introduction

Apatite containing average 0.1–0.8% rare earth oxides is the main source of phosphate fertilizers and phosphoric acid. When apatite is leached with HNO_3, all the rare earths substituted in the apatite lattice for calcium ions are dissolved and a variety of processes are available for their recovery [1–4]. Tributyl phosphate (TBP) was employed to recover rare earths from nitric acid leach solution of apatite, but it is difficult to separate rare earths from Ca^{2+}, PO_4^{3-} effectively with TBP because all of them can be extracted by TBP [5]. So, it is necessary to separate RE(III) from Ca^{2+} and PO_4^{3-} with another extractant, for example, Cyanex923 [6]. Other than this, due to the high water-solubility of TBP (0.28 g/L), the raffinate containing extractant will lead environment pollution.

As an organphosphorus ester, dimethyl heptyl methyl phosphonate $CH_3P(O)(OC_8H_{17})_2$ (P_{350}, B), which has lower water-solubility (~0.01 g/L) compared with TBP, can extract rare earth ions from nitrate media [7]. We chose apatite come from west of Egypt as working sample, studied the influences of phase ratio, stage number, acidity and salting-out agent on extractabilities. The results show that rare earths can be separated with P_{350} from Ca, P, Fe and other impurities effectively. A new process is proposed to recover rare earths from apatite without interfering with the normal route for fertilizer production using solvent extraction with P_{350}.

Mixed rare earth oxides (REO) of which purity is more than 95% with yield over 98% can be obtained.

2. Experimental

2.1. Reagents

P_{350} was kindly supplied by Shanghai Institute of Organic Chemistry without purification before using; kerosene was commercial grade and all other reagents used were of analytical grade.

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doi:10.1016/j.jallcom.2004.12.119

2.2. Analysis

All of elements were analyzed by inductively coupled plasma (ICP–AES/MS) except fluorine, which was analyzed by an ion electrode; the acidity was determined by titration against 0.1025 M NaOH solution using phenolphthalein as indicator.

2.3. Dissolution

The apatite-working sample was dissolved in 20% (v/v) nitric acid solution at 60–70 °C while agitating and the slurry was filtered to remove the insoluble part.

2.4. Separation of the rare earths

The organic phase was composed of P_{350} and kerosene; it should be saturated with 1 mol/L HNO_3. The feed consisted of nitric acid leaching liquor of apatite and salting-out agent. The acidity of feed was adjusted to $[H^+] = 0.4$ mol/L with MgO or NH_3 before countercurrent extraction. Rare earths were extracted with P_{350} and the loading organic phase was scrubbed with 3 mol/L NH_4NO_3 solution to remove the impurities extracted with RE^{3+}. RE^{3+} was afterwards stripped with 0.01 mol/L HNO_3, the stripping solution was then subjected to precipitation of rare earths with 10% $H_2C_2O_4$ solution. All of extraction and stripping experiments were performed in room temperature. Finally, the precipitate was washed with 1% $H_2C_2O_4$ solution and ignited at 700–800 °C to get an oxide concentrate.

The raffinate was mainly composed of NH_4NO_3, $Ca(NO_3)_2$ and $(NH_4)_3PO_4$. For produce the fertilizer, $Ca(NO_3)_2$ can be removed by cooling crystal and centrifugation. Potassium salt was added to get NPK fertilizer products.

3. Results and discussion

3.1. Analysis

The rare earth independent mineral was not found in apatite sample and RE^{3+} enter into the crystal lattice of calcium phosphate in isomorphous substitution for Ca^{2+}. Table 1 shows the typical component of apatite.

Table 1
Typical chemical composition of apatite-working sample

Elements	Content (mg/g)
Ca	269
Fe	28
Mg	5.4
Al	1.5
Mn	1.1
P	100
S	62
F	29.3
Si	30.0
La	0.22
Ce	0.38
Pr	0.051
Nd	0.26
Sm	0.045
Eu	0.012
Gd	0.053
Tb	0.008
Dy	0.042
Ho	0.009
Er	0.039
Tm	0.004
Yb	0.024
Lu	0.004
Y	0.32
Sc	0.020
Th	0.006
U	0.029

3.2. Dissolution

The main chemical reaction that occurs during dissolving apatite with nitric acid can be represented as:

$$Ca_{10}(PO_4)_6F_2 + 20HNO_3 \rightarrow 6H_3PO_4 + 10Ca(NO_3)_2 + 2HF \qquad (I)$$

All the lanthanides substituted in the apatite lattice for calcium ions were dissolved. The leaching temperature did not influence the leaching efficiency of rare earths, but higher temperature is advantageous to the volatilization of S and F. $CaSO_4$ crystal will separate out at high SO_4^{2-} concentration, it can lead the loss of lanthanides that are present in isomorphous with Ca^{2+} in the gypsum. When the leaching temperature was more than 60 °C, almost complete lanthanides recovery can be attained and most of fluorine volatilised as HF; so, defluorination is unnecessary. In this condition, more than 60% of sulphur volatilised, the typical SO_4^{2-} concentration less than 0.04 M. Table 2 shows the typical component of nitric acid leaching liquor of apatite.

3.3. Separation of the rare earths

3.3.1. Extraction mechanism

As an organphosphorus ester, P_{350} can extract rare earth ions (RE^{3+}) from nitrate media according to the following reaction:

$$RE^{3+} + 3NO_3^- + 3B = RE(NO_3)_3{}^{\bullet}3B \qquad (II)$$

Table 2
Typical component of nitric acid leaching liquor of apatite

Elements	Concentration (mg/L)
Ca	12800
Fe	1325
Mg	325
P	5150
S	1128
F	22.3
REEs	72.4

With the increase of aqueous nitrate concentration, the extraction will be enhanced.

3.3.2. Effect of phase ratio and acidity on RE(III) extracting

When phase ratio (organic/aqueous phase) more than 1:1, almost complete RE^{3+} can be extracted into organic phase in a single stage. More than 98% of lanthanides were extracted into organic phase while more than 97.5% of Ca^{2+}, 99.9% of Mg^{2+}, 98.5% of $PO_4{}^{3-}$ and 99.0% of Fe stayed in the raffinate with six stages countercurrent extraction process when phase ratio = 0.5.

Due to the competitive extraction between HNO_3 and RE^{3+}, the influence of HNO_3 concentration to D is complex. The increase of HNO_3 concentration will decrease the effective concentration of P_{350} due to the formation of hydrogen bonding between H^+ and O in P_{350}. The extraction percentage increased with the decrease of feed acidity. But precipitate will form when $[H^+] < 0.3$ mol/L; so, the acidity of feed was controlled to 0.4 mol/L by adding MgO. Fig. 1 shows the effect of acidity of feed to RE(III) extracting.

3.3.3. Effect of salting-out agent on RE(III) extracting

The salting-out effect of NH_4NO_3, $NaNO_3$, $LiNO_3$, $Mg(NO_3)_2$, $Zn(NO_3)_2$, $Fe(NO_3)_3$ and $Al(NO_3)_3$ have been investigated. The results showed that in equal $NO_3{}^-$ concentration, the salting-out effect increased with the order: $Li^+ < NH_4{}^+ < Na^+ < Mg^{2+} < Zn^{2+} < Fe^{3+} < Al^{3+}$.

For the advantage of fertilizer production, NH_4NO_3 was selected to as salting-out agent. Fig. 2 shows the effect of aqueous NH_4NO_3 concentration on RE(III) extracting.

3.3.4. Dependence of scrubbing efficiency on phase ratio

The dependence of scrubbing efficiency on phase ratio are shown in Table 3. The impurity loaded in organic phase can be removed by scrubbing with 3 mol/L NH_4NO_3 solution, while the scrubbing process will lead the loss of lanthanides loaded in organic phase. When phase ratio = 10, the scrubbing of three stages can decrease the $[Ca^{2+}]$ of organic phase to 10.2 mg/L $[Ca^{2+}]$ in organic phase after five stages scrubbing can be decreased to 5.1 mg/L.

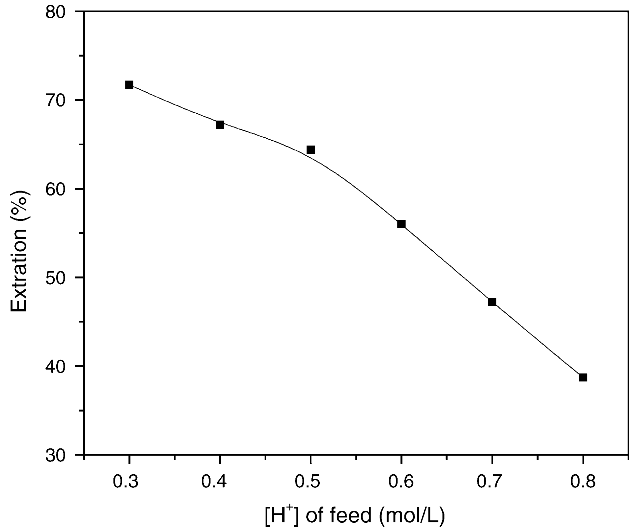

Fig. 1. Effect of acidity on RE(III) extracting, organic/aqueous phase ratio = 1, organic phase: 50% P_{350} ~ kerosene $[REEs]_{aq}$ = 56.7 mg/L.

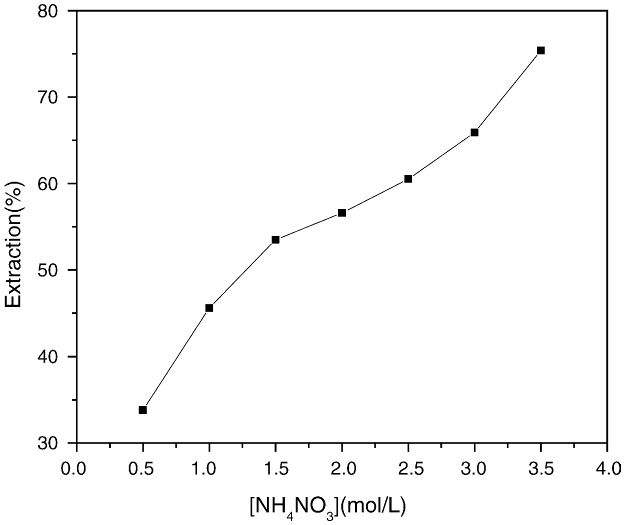

Fig. 2. Effect of aqueous NH_4NO_3 concentration on RE(III) extracting, organic/aqueous phase ratio = 1, organic phase: 50% P_{350} ~ kerosene $[REEs]_{aq}$ = 56.7 mg/L.

Table 3
Dependence of scrubbing efficiency on phase ratio

Phase ratio	$[Ca^{2+}]$ of loading organic phase (mg/L)	Loss percentage of REEs of organic phase
12	64.0	0.2
10	54.0	0.8
8	44.3	2.3
6	28.8	3.6
4	22.2	4.3

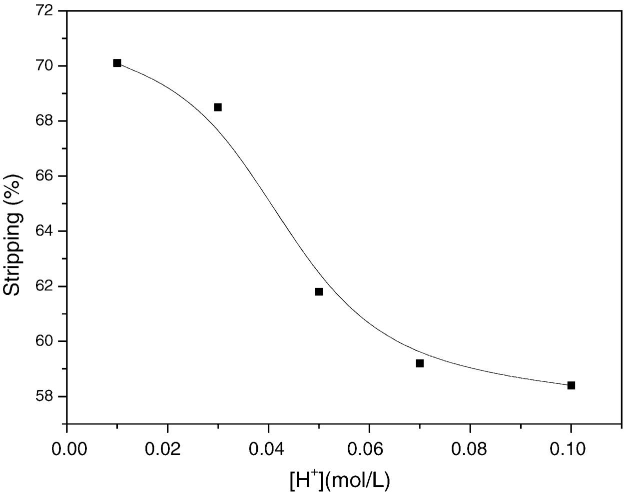

Fig. 3. Influence of acidity on stripping, organic/aqueous phase ratio = 1, organic phase: 50% P_{350} ~ kerosene $[REEs]_{org}$ = 122.4 mg/L.

Table 4
Analysis results of REO

Elements	Content (%)
Ca	2.3
Fe	0.54
Mg	0.76
P	–
S	–
REEs	97.3

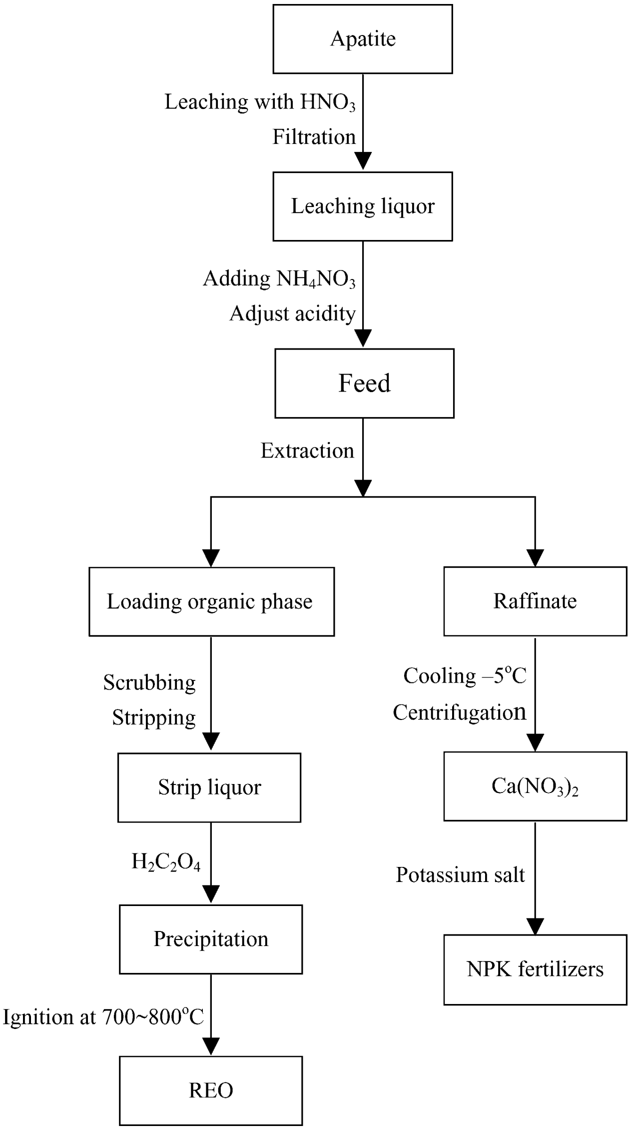

Fig. 4. The general flowsheet for recovery of lanthanides from apatite with P_{350}.

3.3.5. *Influence of phase ratio and acidity on stripping*

HNO_3 was selected to strip RE^{3+} from loading organic phase. The stripping percentage decreased with the increase of organic/aqueous phase ratio. Fig. 3 shows the influence of acidity on stripping.

3.3.6. *Analysis results of REO*

The stripping solution was subjected to precipitation of rare earths with 10% $H_2C_2O_4$ solution and the precipitate was then washed with 1% $H_2C_2O_4$ solution and ignited at 700–800 °C to get an oxide concentrate. Table 4 shows the analysis results of REO, the purity of REO being more than 96.0%.

4. The general flowsheet for recovery of lanthanides from apatite

Fig. 4 shows the general flowsheet for recovery of lanthanides from apatite using solvent extraction with P_{350}. Mixed rare earth oxides (REO) of which purity was more than 95% with yield over 98% can be obtained without interfering with the normal route for fertilizer production. The REO can be followed by the individual rare earth elements separation with P_{507} extraction [8].

Acknowledgements

This project is supported by Nation Program entitled ‘Basic Research of Rare Earths’ (G1998061301), National Natural Science Foundation of China (20371046) and National ‘863’ Project (2002AA647070).

References

[1] F. Habashi, J. Chem. Technol. Biotechnol. 35A (1985) 5–14.
[2] M.M. Aly, N.A. Mohammed, Hydrometallurgy 52 (1999) 199–206.
[3] J.S. Preston, P.M. Cole, W.M. Craig, A.M. Feather, Hydrometallurgy 41 (1996) 1–19.
[4] C. Koopman, G.J. Witkamp, Hydrometallurgy 58 (2000) 51–60.
[5] Y.Y. Li, M.L. Gong, Y.S. Yang, Chemistry of Inorganic Separation Process, Zhongshan University Press, Guangzhou, 1993, p. 51.
[6] A.W. Al-Shawi, S.E. Engdal, O.B. Jenssen et al., ISEC 2002, 1064–1069.
[7] G.X. Xu, C.Y. Yuan, Solvent Extraction of Rare Earths, Science Press, Beijing, 1987, p. 195.
[8] D.Q. Li, Z.H. Wang, W.Z. Song, et al., Hydrometallurgy’94, Chapman & Hall, London, 1994, p. 627.