Y. LI, J. G. HE, X. X. XUE, H. Q. RU, X. W. HUANG, H. YANG

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EXRACTION AND SEPARATION OF CERIUM(IV)/FLUORINE IN FLUORIDE-BEARING CERIUM SULFATE SOLUTION WITH FLUORIDE COORDINATION AGENT

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In this paper the extraction and separation of cerium/fluorine in fluoride-bearing cerium sulfate solution with fluoride coordination agent has been studied. The UV-vis spectra suggest that Zr^{6+} and Al^{3+} can scrub the F^- from $[CeF_2]^{2+}$ complex. The separation and conductivity studies show that aluminum salt is the most suitable fluoride coordination agent, and an ion-exchange reaction is involved between Ce^{4+}/ $[CeF_2]^{2+}$ and hydrogen ion.

Keyword: fluorine, cerium, separation, fluoride coordination agent

INTRODUCTION

Rare earth has been widely used in metallurgy, electronic industry, nuclear industry, agriculture and other fields due to its unique optical, electrical, magnetic properties. There are about 200 rare earths (RE) minerals worldwide, including halides, carbonates, oxides, phosphates, silicates, etc [1]. Bastnaesite ($ReCO_3F$, Re = Rare earths) is one of the most important mineral resources containing about 75% combined rare earth oxides (REO) especially light rare earth elements [2]. At present, the "acid leaching - solvent extraction" process is considered to be the main technology for bastnaesite treatment. Hydrochloric and sulfuric acids can be used as leaching reagents mostly. The hydrochloric acid leaching process has been gradually phased out because of the backwardness and serious environmental pollution. The sulfuric acid leaching process can dissolute almost all of Ce^{4+}, RE^{3+}, F^- and Th^{4+}, and it is considered to be more advanced technology for bastnaesite utilization[3,4]. Bastnaesite theoretically contains about 7 ~ 9 % fluorine. The fluoride mainly exists in the form of $[CeF_2]^{2+}$ complex in sulfuric acid system because of its high electronegativity and small ionic size, which makes it difficult to separate F^- and Ce^{4+}, and also may bring about the formation of the third phase during the subsequent extraction separation of rare earths [5, 6]. Therefore, the key point of sulfuric acid leaching process is to eliminate the influence of fluorine. Lots of investigations about defluorination in the smelting of bastnaesite have been reported [7 ~ 9].

In this study, taking fluoride-bearing cerium sulfate solution as the research object, fluoride coordination agent was added into the solution to scrub the fluoride from $[CeF_2]^{2+}$, resulting in the free Ce^{4+} in solution. Then the resultant solution was mixed with organic phase to extract Ce^{4+}, leading to the separation of cerium and fluorine. The objectives of this paper are mainly to eliminate the influence of fluorine on the extraction of rare earths and carry out exploration research on the high efficient separation of rare earths.

EXPERIMENTAL

H_2SO_4(A.R. 98 %), NaF, $Ce(SO_4)_2$•$4H_2O$, etc. of analytical grade were purchased from Shenyang Guoyao Group Chemical Reagent Co., Ltd. HDEHP and kerosene was supplied by Shanghai Laiyashi Chemical Co., Ltd. The organic phase was diluted with kerosene to the required concentration, and the kerosene was sulfonated before use. The fluoride-bearing cerium sulfate solution was prepared by dissolving $Ce(SO_4)_2$•$4H_2O$ and NaF in dilute sulphuric acid. Ce^{4+} concentration was determined by titration with standard $(NH_4)_2Fe(SO_4)_2$ using sodium diphenylamine sulfonate as indicator. F^- was determined by fluoride-selective electrode method.

UV-2550 uv-vis spectrophotometer was employed to detect the absorbance of the solution. MP515 precision conductivity meter was used to determine the conductivity of the solution.

All separation studies were carried out by adding a certain amount of fluoride coordination agent into the fluoride-bearing cerium sulfate solution and the aqueous was well-mixed. Then equal volumes (20 mL) of aqueous and organic solutions was mixed and shaken in equilibrium tubes using a mechanical shaker for 20 min at room temperature, after that the aqueous phase was analyzed after centrifugal separation. The concentration

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Y. Li, J. G. He, X. X. Xue, H. Q. Ru, H. Yang School of Material and Metallurgy, Northeastern University, Shenyang, Liaoning, China.
X. W. Huang, National Engineering Research Center for Rare Earth Materials, General Research Institute for Nonferrous Metals, and Grirem Advanced Materials Co., Ltd., Beijing,China

in the organic phase was obtained by mass balance. The separation coefficient $\beta_{Ce/F}$ was obtained as following expression:

$$\beta_{Ce/F} = ([Ce]_o \times [F]_a) / ([Ce]_a \times [F]_o)$$

where $[Ce]_o$ and $[F]_o$ (mol / l) are the equilibrium concentrations of cerium and fluoride in organic phase, and $[Ce]_a$ and $[F]_a$ (mol / l) are the equilibrium concentrations of cerium and fluoride in aqueous phase.

RESULTS AND DISCUSSION

The $Al(NO_3)_3$, H_3BO_3, NH_3VO_3 and $Zr(NO_3)_4$ were chosen as the fluoride coordination agents. The UV-vis spectra of solutions are seen in Figure 1. It is seen from the UV absorption spectrum of Ce solution that the maximum absorption wavelength is around 320nm, and a strong absorption also appears in the range of 200 - 250 nm. A clear blue shift (320 nm → 310 nm) occurs in the UV absorption spectrum of F-Ce solution, which is due to that F^- coordinates with Ce^{4+} to form $[CeF_2]^{2+}$ complex in sulfuric acid solution. The absorption spectra of Ce-F-Zr and Ce-F-Al solutions are similar to that of Ce solution with the maximum absorption wavelengths around 320 nm and good absorption in the range of 200 - 250 nm. This is probably attributed to the good stability of zirconium fluoride complexes $[ZrF_n]^{(4-n)}$ and aluminum fluoride complexes $[AlF_n]^{(3-n)}$. The Zr^{6+} and Al^{3+} can scrub the F^- from $[CeF_2]^{2+}$ complex, leading to the separation of cerium and fluorine. However, the absorption spectrum of Ce-F-B solution is the same as that of Ce-F solution, and the maximum absorption wavelength of Ce-F-V solution is around 300 nm, showing that the separation effects of H_3BO_3 and NH_3VO_3 are poorer than that of $Zr(NO_3)_4$ and $Al(NO_3)_3$. Figure 2 shows the separation coefficients obtained of different fluoride coordination agents. It is found that the best separation effect is obtained when using $Al(NO_3)_3$ as fluoride coordination agent. Although the Zr^{6+} and Al^{3+} can both coordinate with F^- strongly as shown in Figure 1, the $[ZrF_n]^{(4-n)}$ complex ions are easily to be extracted into organic phase during extraction process, leading to the poor separation effect. Therefore, aluminum salt is a suitable fluoride coordination agent for the separation of cerium and fluorine in fluoride-bearing cerium sulfate solution.

The $NaAlO_2$, $Al(NO_3)_3$, $Al_2(SO_4)_3$ and $AlCl_3$ were chosen as the fluoride coordination agents. The obtained results in Figure 3 show that that the separation coefficients of cerium and fluorine significantly increase with the addition of aluminum salts. The separation effects of $NaAlO_2$ and Al $(NO_3)_3$ are better than that of $Al_2(SO_4)_3$ and $AlCl_3$. This can be explained by the reducibility of chloride ion which can reduce Ce^{4+} to Ce^{3+} in the organic phase, leading to the loss of cerium by forming CeF_3 particles which go into the aqueous phase. Besides, sulfate ion may compete with fluoride ion for the aluminum complexes since sulfate ion is partially inner-sphere complex forming species[10]. Based on the above analysis, $NaAlO_2$ and $Al(NO_3)_3$ are most suitable for fluoride coordination reagents to separate cerium and fluorine.

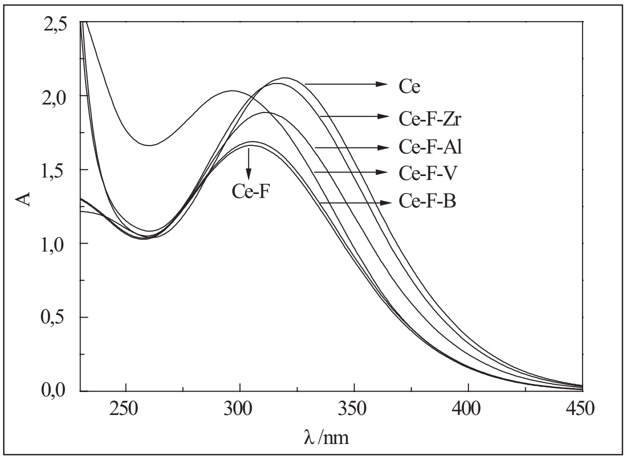

Figure 1 The UV-vis spectra of different solutions before extraction ($[Ce^{4+}]$ = 0,04 mol/l, n_F/n_{Ce} =1,8, n_F/n_M = 2, $[H^+]$ = 0,5 mol/l, M is fluoride coordination agent)

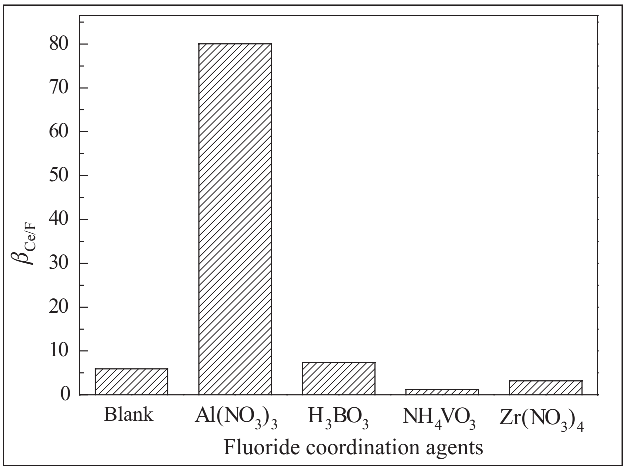

Figure 2 Effect of different fluoride coordination agents on the separation of cerium and fluorine ($[Ce^{4+}]$ = 0,04 mol/l, n_F/n_{Ce} = 1,8, n_F/n_M = 2, $[H^+]$ = 0,5 mol/l, [HDEHP] = 0,1 mol·L^{-1})

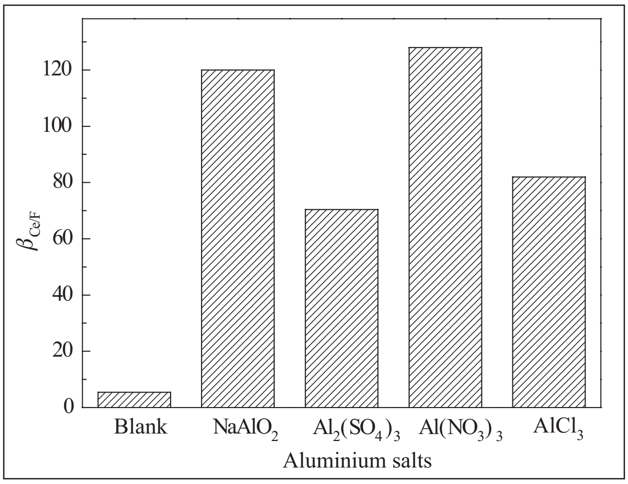

Figure 3 Effect of different aluminum salts on the separation of cerium and fluorine ($[Ce^{4+}]$ = 0,02 mol/l, n_F/n_{Ce} = 1,8, n_F/n_{Al} = 2, $[H^+]$ = 0,24 mol/l, [HDEHP] = 0,13 mol·L^{-1})

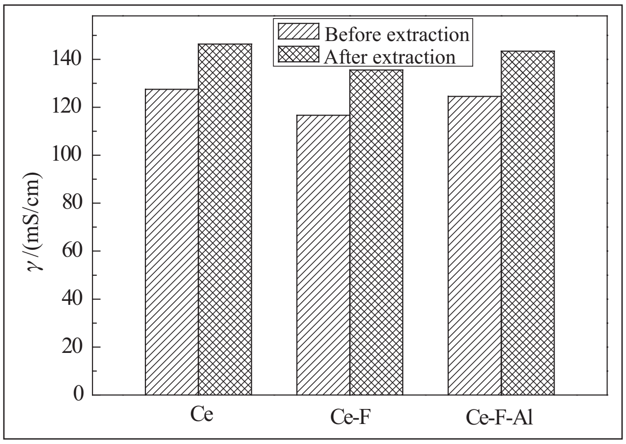

Figure 4 The conductivities of Ce, Ce-F and Ce-F-Al solutions before and after extraction

Figure 4 shows the conductivities of Ce, Ce-F and Ce-F-Al solutions before and after extraction. Because of the high ion charge number of Ce^{4+}, the conductivities of solutions are mostly depend on Ce^{4+}. It is evident from Figure 4 that the conductivity of Ce-F solution is lower than the conductivities of Ce and Ce-F-Al solutions. The reason is that Ce will complex with F to form $[CeF_2]^{2+}$ ions in sulfuric acid media, so the conductivity decreases with the reduction of ion charge number and the increase of ionic radius. The conductivities of Ce and Ce-F-Al solutions are close showing that Al^{3+} has scrubbed the F^- from $[CeF_2]^{2+}$ complex and cerium exists as free Ce^{4+} in solution. Furthermore, the conductivities of solutions are both increase after extraction. The reason may be that the extraction reactions of Ce, Ce-F solutions from sulfuric acid media with HDEHP can be expressed as Eqs.(1) and (2)[11]. An ion-exchange reaction takes place between $Ce^{4+}/[CeF_2]^{2+}$ and hydrogen ion. The ion mobility and conductivity of hydrogen ion are high because the current conduction of hydrogen ion is depend on hydrogen bond, which is much faster than other ion.

$$Ce^{4+}_{(a)} + (HA)_{2(o)} \rightarrow CeA_{4(o)} + 4H^+_{(a)} \quad (1)$$

$$[CeF_2]^{2+}_{(a)} + (HA)_{2(o)} \rightarrow CeF_2A_{2(o)} + 2H^+_{(a)} \quad (2)$$

CONCLUSIONS

In this study, the extraction and separation of cerium/fluorine in fluoride-bearing cerium sulfate solution with fluoride coordination agent has been investigated. The conclusions drawn from the studies can be summarized as:

The UV-vis spectra suggest that Zr^{6+} and Al^{3+} can scrub the F^- from $[CeF_2]^{2+}$ complex, and aluminum salt is the most suitable fluoride coordination agent for the separation of cerium and fluorine in fluoride-bearing cerium sulfate solution.

The $NaAlO_2$ and Al $(NO_3)_3$ are most suitable for fluoride coordination agents. The conductivity study shows an ion-exchange reaction between Ce^{4+} / $[CeF_2]^{2+}$ and hydrogen ion in extraction process.

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REFERENCES

[1] G. X. Xu, Rare Earths, second ed., Metallurgical Industry Press, Beijing, 1995.
[2] G. C. Zhang, X. W. Huang, Chin. J. Rare Met. 21 (1997) 3, 193-199.
[3] S. L. Zhao, C. G. He, Z. J. Cao, Y. Liu, F. Zhao, Chin. Rare Earths. 24 (2003) 4, 32-35.
[4] R. M. Sawant, R. K. Rastogi, M. A. Mahajan, N. K. Chaudhuri, Talanta 43 (1996) 89-94.
[5] J. Qiao, C. R. Zhang, S. G. Liu, X. K. Hao, Chin. Rare Earths. 18 (1997) 64-67.
[6] Z. F. Zhang, H. F. Li, F. Q. Guo, S. L. Meng, D. Q. Li, Sep. Purif. Technol. 63 (2008) 348-352.
[7] Meenakshi, R. C. Maheshwari, J. Hazard. Mater. 137 (2006) 456-463.
[8] X. M. Dou, D. Mohan, C. U. Pittman Jr., S. Yang, Chem. Eng. J. 198-199 (2012) 236-245.
[9] R. Chitrakar, S. Tezuka, A. Sonoda , K. Sakane, K. Ooi, T. Hirotsu, J. Colloid Interface Sci. 97 (2006) 426-433.
[10] S. K. Swain, S. Mishra, T. Patnaik, R. K. Patel, U. Jha, R. K. Dey, Chen. Eng. J. 184 (2012) 72-81.
[11] M. L.Toullec, C. J. Simmons, J. H.Simmons, J. Am. Ceram. Soc. 71 (1988) 219-224.

Note: For English language is responsible the lecturer from Northeastern University, Shenyang, China