Correlation complexation constants of Ce$^{4+}$ and F$^-$

Ying Jiang$^*$, Xuemei Wang$^1$, Yunzhu Chen$^1$ and Lichao Nengzi$^1$

$^1$School of Resource and Environment, Xichang University, Xichang 615000

*Corresponding author e-mail: jy1123email@163.com

Abstract. Measured CeFn (n=1, 2, 3) complexation constant and solubility product constant of CeF$_4$ and Na$_2$CeF$_6$ by ICP-AES and UV spectrophotometer, when Ce$^{4+}$ and F$^-$ complexation reaction in water medium and nitric acid medium respectively, and the effects of Re$^{3+}$ and nitric acid concentration on Ce$^{4+}$ and F$^-$ complexation reaction were studied. The experimental results show that the first-order complexation constant of Ce$^{4+}$ and F$^-$ is CeF$_3$$^+$$=$6.94$*$10^6, the second-order complexation constant is CeF$_2$$^{2+}$$=$$4.541$*$10^{11}$, and the third-order complexation constant is CeF$_3$$^{3+}$$=$$6.232$*$10^{14}$. Compared with the complexation reaction of Ce$^{4+}$ and F$^-$ in water medium and nitric acid medium, the complexation reaction of Ce$^{4+}$ and F$^-$ in nitric acid medium is better. Re$^{3+}$ appears, which affects the complexation reaction between Ce$^{4+}$ and F$^-$. When in nitric acid medium, the higher the concentration of nitric acid, the more unfavorable the complexation of Ce$^{4+}$ and F$^-$. The study of the relevant physical constants of Ce$^{4+}$ and F$^-$ in this paper can be helpful for the separation of Ce$^{4+}$ and F$^-$, enrich the physical and chemical information of rare earth elements, and provide the basic theoretical basis for the rare earth fluoride that is difficult to be separated and recovered from the tailings, so as to reduce the harm to the soil environment.

1. Introduction

With the unique electronic layer structure, rarely are earth elements widely used in more than 40 industries in 13 fields, such as high-tech materials, electronic information, petrochemical and national defense. About 70% of the world's rare earths are produced from fluorocarbon cerium ore[1], and fluorine, due to its strong chemical binding ability, it makes the process of "fluorine/rare earth separation" extremely difficult, which is the main source of environmental pollution and resource waste in the wet smelting of rare earth ore. At present, "oxidizing roasting - hydrochloric acid leaching process" could take place of the mainstream of bastnaesite leaching process, which the process is less investment, low cost, but low purity cerium oxide, hydrochloric acid leaching process of Ce$^{4+}$, Th, F into residue, which is needed to through alkali conversion processing, and ignored the existence of fluorine in bastnaesite for serious influence of rare earth leaching process, and the process of fluorine into the wastewater discharge in the form of NaF, fluorine in order to remove impurities from the ore, not only are the natural resources wasted, but also the emissions of fluorine could cause secondary pollution to the environment, the whole process of Th, Fhas not been considered comprehensive recycling, scattered into the waste water and waste residue, the environment is seriously polluted, resulting in the "three big" problems, including "big consumption, big pollution and big emission" [2]. Wang liangshi et al. [3] took fluorocarbon cerium ore oxidized roasting and sulfuric acid leaching to obtain the solution containing fluorine, thorium and cerium sulfate as raw materials, and used HEH(EHP) to extract and separate cerium, fluorine and thorium. In the extraction process, F forms
complexes [CeF\(_{4-x}\)]\(_4^{-x}\) and [ThF\(_{4-x}\)]\(_4^{-x}\) with Ce\(^{4+}\) and Th\(^{4+}\) respectively. In some cases, Ce\(^{4+}\), which is complexing with F\(^-\) produces [CeF\(_6\)]\(_2^-\) which can also form Na\(_2\)CeF\(_6\) similar to cryolite Na\(_3\)AlF\(_6\) [4]. In special cases, Ce\(^{4+}\) can also form the complex form of [CeF\(_9\)]\(_5^-\) with F\(^-\), but due to the presence of other rare earth elements in the ore, it is very difficult to form this shape [7].

The study on the related physical which constants of Ce\(^{4+}\) and F\(^-\) is not only helpful to the separation of Ce\(^{4+}\) and F\(^-\), but also it lays a foundation for the study of the related physical which constants of Fe\(^{3+}\), Th\(^{4+}\) and F\(^-\). Because fluorine is not only a pollutant that can be limited and discharged, but also it is a serious interference factor for the extraction and separation of rare earth and a limited impurity for the purity of the product, fluorine is also a precious resource. Therefore, some theoretical basis for the extraction and separation of Ce\(^{4+}\)/F can be provided by the study on the relevant physical which constants of Ce\(^{4+}\) and F\(^-\). The economical and efficient recycling of fluorine and thorium is the key to green smelting of rare earth by means of the wet process, and it is also an important prerequisite for preparing high purity rare earth. During 1996-2005, rare earth production is turned to "control of fluorine thorium and clean production", F and Th were integrated into the grouping system, and new rare earth extraction technologies emerged one after another [5]. A series of organic grouping reagents were developed with rare earth sulphuric acid extract containing fluorine with raw material. P507 was used to be grouping reagent, which was divided into two groups: RE\(^{3+}\), Ce\(^{4+}\), F\(^-\) and Th\(^{4+}\). As a grouping agent, the impurity quality of cerium products and lanthanum-rich aqueous solutions are decreased significantly, and the trend of fluorine and thorium pollutants were controlled. However, F and Th did not be recovered in the grouping system, and the extraction capacity of P507 was easy to emulsify lowly. Li deqian et al. used N1923 and Cyanex923 to be grouping agents and they were divided into RE\(^{3+}\), Ce\(^{4+}\), Th\(^{4+}\) and F\(^-\) four components by extraction and reverse extraction. The method has high rare earth yield, but F\(^-\) has not been recovered by using boric acid as masking agent, and the cost of grouping reagent is high. Huang Xiaowei et al. used P204 to be the grouping agent, and after extraction and reverse extraction, it was divided into four components: RE\(^{3+}\) and Ce\(^{4+}\), Th\(^{4+}\), F\(^-\), etc., which reduced the cost of organic extractant and controlled the pollution of Th\(^{4+}\) and F\(^-\). FeF\(_n\)(n=1,2,3,5)pK stability was 5, 8, 9.30, 12.06 and 15.77, and ThF\(_y\)(y=1,2,3,4) pK stability was 8.44, 15.08, 19.80 and 23.20. However, there was no study on the stability constant change of Ce\(^{4+}\) and F\(^-\) under the influence of acidity and Cl\(^-\), SO\(_4\)\(^2-\) and NO\(_3\)\(^-\). By referring to the literature, there are few reports on the multiple complexes of REF and CeF\(_m\) and their stability constants. There are only studies on the complexation behavior of CeF\(^{2+}\), the K= 2.8×10\(^{10}\). There are also Ksp reports of REF\(_3\), but there is no study on the K stability change of these complexes under the influence of acidity and other conditions. Although there are many studies on the physical and chemical behavior of fluorine in the extraction of rare earth, they are mainly focused on the physical and chemical behavior of fluorine in the process of activation of rare earth ore, extraction of rare earth and separation of rare earth and its pollution control. For example, the graded complexation constant and conditional stability constants of MF6b-; MFm and Na\(_{m0}\)MF\(_6\) Ksp, conditional Ksp, etc.. Not only can these complexing constants enrich the physical and chemical information of rare earth elements, but also provide the basic theoretical basis for the rare earth fluorides that are difficult to be separated and recovered from tailings, thus it can reduce the harm to the soil environment.

2. Materials and methods

2.1. Instrument
ICP-AES, UV Spectrophotometer

2.2. Reagent
Ce(SO\(_4\))\(_2\); La\(_2\)O\(_3\); Nd\(_2\)O\(_3\); FeCl\(_3\); HF; HNO\(_3\); HF and HNO\(_3\) are analysis of pure.
2.3. Experiment method
The CeFn (n=1, 2, 3) complexation constant is determining if a certain amount of hydrofluoric acid is added to the solution of cerium, the color of the solution of cerium will gradually become lighter. At this time, Ce\(^{4+}\) and F\(^{-}\) form a complex, so the determination is carried out by spectrophotometry. Ce\(^{4+}\) solution of 0.0567mol/L and HF solution of 0.0567mol/L were prepared to maintain the total amount of Ce\(^{4+}\) and F\(^{-}\). The absorbance was determined by adding different proportions of solution. Moreover, the influence of different trivalent rare earth ions on its complexation constant was considered, namely, the Nd\(^{3+}\), Pr\(^{3+}\) and La\(^{3+}\) solutions of 0.01mol/L were prepared, and their absorbance was determined after adding different amounts of trivalent rare earth solutions. A small amount of cerium tetrafluoride in a beaker is weighed, a certain amount of dilute nitric acid is added, which is heated and stirred on a magnetic stirrer, after a certain time, the concentration of Ce\(^{4+}\) and F\(^{-}\) is measured in the solution, and its Ksp is calculated according to its concentration.

3. Results and discussion

3.1. Determination of CeFn (n=1, 2, 3) complexation constant
At the wavelength of 472nm, the optical density of Ce\(^{4+}\) and F\(^{-}\), which is complexed solution in nitric acid solution was measured, and the mean value of the parallel sample was obtained. It has been shown in figure 1, the highest point indicates that the proportion is formed by Ce\(^{4+}\) and F\(^{-}\) is 1:2. In the solution system of Ce\(^{4+}\) and F\(^{-}\), there are several complexation equilibria:

\[
\begin{align*}
\text{Ce}^{4+} + F^{-} & \leftrightarrow \text{CeF}^{3+} \quad \ldots \,(1); \\
\text{CeF}^{2+} + F^{-} & \leftrightarrow \text{CeF}^{2+} \quad \ldots \,(2); \\
\text{Ce}^{4+} + F^{-} & \leftrightarrow \text{CeF}^{3+} \quad \ldots \,(3); \\
\text{Ce}^{4+} + F^{-} & \leftrightarrow \text{CeF}^{2+} \quad \ldots \,(4); \\
\text{Ce}^{4+} + F^{-} & \leftrightarrow \text{CeF}^{2+} \quad \ldots \,(5); \\
\text{Ce}^{4+} + F^{-} & \leftrightarrow \text{CeF}^{2+} \quad \ldots \,(6); \\
\text{Ce}^{4+} + F^{-} & \leftrightarrow \text{CeF}^{2+} \quad \ldots \,(7); \\
\text{Ce}^{4+} + F^{-} & \leftrightarrow \text{CeF}^{2+} \quad \ldots \,(8).
\end{align*}
\]

Select points under the corresponding proportion and calculate according to the formula:

\[
\beta(CeF_{n}^{4+}) = \left( \frac{\Delta A_1}{\Delta A_2} \cdot [Ce^{4+}] \right)[\text{T}^{n} - n \cdot \frac{n!}{\alpha H^{+} \cdot \Delta A_1 \cdot [Ce^{4+}] \cdot [H^{+}]^{n}}]
\]

| Table 1. Absorbance of the highest point ratio of 1:2 |
|---------------------------------|--------|--------|---------|
| Ce\(^{4+}\)/F\(^{-}\) | A1     | A2     | \(\Delta A_1\) |
| 1     | /      | 0.866  | 0.866   |
| 2     | 4/1    | 0.717  | 0.597   | 0.12 |
| 3     | 3/2    | 0.561  | 0.352   | 0.209 |
| 4     | 1/1    | 0.481  | 0.224   | 0.257 |
| 5     | 2/3    | 0.394  | 0.118   | 0.276 |
| 6     | 1/2    | 0.344  | 0.065   | 0.279 |
| 7     | 1/3    | 0.271  | 0.043   | 0.228 |
| 8     | 1/4    | 0.218  | 0       | 0.218 |
| 9     | /      | 0      | 0       | 0     |
Figure 1. Formation of CeF$_2$ solution

Table 2. Absorbance of the highest point ratio of 1:1

| Ce$^{4+}$/F | A1  | A2  | △A1  |
|------------|-----|-----|------|
| 1          | /   | 0.799 | 0.799 | 0 |
| 2          | 4/1 | 0.600 | 0.502 | 0.098 |
| 3          | 3/2 | 0.418 | 0.225 | 0.193 |
| 4          | 1/1 | 0.332 | 0.105 | 0.227 |
| 5          | 2/3 | 0.249 | 0.051 | 0.198 |
| 6          | 1/2 | 0.191 | 0.042 | 0.149 |
| 7          | 1/3 | 0.123 | 0.041 | 0.082 |
| 8          | 1/4 | 0.067 | 0     | 0.067 |
| 9          | /   | 0     | 0     | 0 |

Figure 2. Formation of CeF$_3^+$ solution

Table 3. Absorbance of the highest point ratio of 1:3

| Ce$^{3+}$/F | A1  | A2  | △A1 |
|------------|-----|-----|------|
| 1          | /   | 1.153 | 1.153 | 0 |
| 2          | 4/1 | 0.937 | 0.794 | 0.143 |
| 3          | 3/2 | 0.674 | 0.504 | 0.170 |
| 4          | 1/1 | 0.559 | 0.354 | 0.205 |
| 5          | 2/3 | 0.328 | 0.101 | 0.227 |
| 6          | 1/2 | 0.298 | 0.041 | 0.257 |
| 7          | 1/3 | 0.272 | 0.007 | 0.265 |
| 8          | 1/4 | 0.201 | 0.001 | 0.200 |
The complexation constant calculated is: $\beta_{\text{CeF}}^{3+}=6.94\times10^6$; $\beta_{\text{CeF}}^{2+}=4.541\times10^{11}$; $\beta_{\text{CeF}}^{3+}=6.232\times10^{14}$.

3.2. Effects of Re$^{3+}$ on the complexation of Ce$^{4+}$ and F$^-$

In the system solution of Ce$^{4+}$ and F$^-$ is added with La$^{3+}$, Nd$^{3+}$ and Pr$^{3+}$, and three kinds of are mixed with ion solution, with Re$^{3+}$ content increased, the absorbance of Ce$^{4+}$ increases gradually, in the add Re$^{3+}$, the solution of the Ce$^{4+}$ and Re$^{3+}$ on F complex competition, causing F with Re$^{3+}$ complexation to make the Ce$^{4+}$ absorbance increase. When the addition amount is the same, different Re$^{3+}$ have different effects on them. This is because the ion radius of La$^{3+}$, Nd$^{3+}$ and Pr$^{3+}$ increases, in turn, the electrostatic force decreases in turn, and the complexing force on F$^-$ weakens in turn, which leads to the weakening of the influence on Ce$^{4+}$.

3.3. Effects of nitric acid concentration on complexation of Ce$^{4+}$ and F$^-$

Adding nitric acid with 0.5mol/L, 1mol/L and 1.5mol/L to the solution, which contains Ce$^{4+}$ and F$^-$, and then measuring its absorbance. It has been shown in figure 5, as the concentration of nitric acid increasing, the absorbance also increases, because there is an equilibrium reaction in the solution: $\text{HF} \leftrightarrow \text{H}^+ + \text{F}^-$, with the increases of acidity, the amount of H$^+$ in the solution also increases, which leads to the left movement of the equilibrium reaction of hydrofluoric acid dissociation, reduces the content of F in the solution, thus reduces the F$^-$ in contact with Ce$^{4+}$ and increases the absorbance.
Figure 5. Effects of different concentrations of nitric acid on the complexation of Ce⁴⁺ and F⁻

3.4. Determination of solubility product constant of CeF₄ and Na₂CeF₆

Put a small amount of CeF₄ with washed and dried and Na₂CeF₆ into a beaker, adding an appropriate amount of nitric acid, and then heating and stirring on a magnetic stirrer. After 6 hours, it is time to filter the supernatant and determine the content of Ce⁴⁺ and F⁻ in the supernatant.

Figure 6. XRD of CeF₄

After the concentration measured by ICP-OAE, its Ksp is calculated as follows:

Table 4. Results of Ksp calculation

|                  | Water medium  | Nitric acid medium |
|------------------|---------------|--------------------|
| CeF₄             | 1.753 × 10⁻³¹ | 1.945 × 10⁻²¹      |
| Na₂CeF₆          | 1.831 × 10⁻¹³ | 3.179 × 10⁻¹¹      |

4. Conclusions
(1) The first-order complexation constant of Ce⁴⁺ and F⁻ is CeF₃⁻ = 6.94 × 10⁶; the second-order complexation constant is CeF₂²⁻ = 4.541 × 10¹¹. The third-order complexation constant is CeF₃⁻ = 6.232 × 10¹⁴. From the successive complexing, which constants of Ce⁴⁺ and F⁻ it can be seen that the complexing constantly keeps increasing, which proves that the complexing ability between Ce⁴⁺ and F⁻ is more stable.

(2) Competing with Ce⁴⁺, Re³⁺ can complicate with F⁻, which can lead to the complexation of part of F⁻ with Re³⁺ to increase the absorbance of Ce⁴⁺. At the same time, the dosage of different Re³⁺ on its influence is also different in phase, which the reason is that La³⁺, Nd³⁺ and Pr³⁺ ion radius increase in turn, reduce the electrostatic force, complexation of F force is abated, leading to weaken the influence
of Ce\textsuperscript{4+}, so Re\textsuperscript{3+} in the solution concentration on the Ce\textsuperscript{4+} and the reaction of F\textsuperscript{-} have a certain influence.

(3) The reaction between Ce\textsuperscript{4+} and F has been greatly influenced by reaction medium. The higher the acidity is, the more unfavorable the complexation between Ce\textsuperscript{4+} and F\textsuperscript{-}. The Ksp of CeF\textsubscript{4} in water medium is 1.753×10\textsuperscript{-31}, the Ksp of Na\textsubscript{2}CeF\textsubscript{6} is 1.831×10\textsuperscript{-13}, and the Ksp of CeF\textsubscript{4} in nitric acid medium is 1.945×10\textsuperscript{-21}, and the Ksp of Na\textsubscript{2}CeF\textsubscript{6} is 3.179×10\textsuperscript{-11}. Therefore, it can be seen that Ksp of CeF\textsubscript{4} and Na\textsubscript{2}CeF\textsubscript{6} in the acid medium is larger than that it is in the water medium and more precipitate in the acid medium.

(4) A basic theoretical basis for the "fluorine/rare earth separation" in rare earth minerals could be provided from the above conclusions, which can also recycle and utilize the rare earth fluoride in the rare earth tailings to reduce the harm of soil environment caused by the presence of rare earth fluoride in the tailings.

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