

REMOVAL OF FLUORIDE FROM FLUORIDE-BEARING CERIUM SULFATE SOLUTION BY HYDROUS ZIRCONIUM OXIDE

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In this paper the removal of fluoride from fluoride-bearing cerium sulfate solution by amorphous hydrous zirconium oxide was studied. The FTIR, SEM, EDS and UV-vis spectra show that fluoride is successfully adsorbed on hydrous zirconium oxide, and cerium exists as Ce^{4+} in solution. The study indicates that it is feasible to separate fluorine and cerium from fluoride-bearing rare earth sulfate solution using hydrous zirconium oxide, and eliminate the influence of fluoride on the extraction separation of rare earths.

Key word: fluoride, cerium, adsorption, hydrous zirconium oxide

INTRODUCTION

It is well known that the bastnaesite is one of the main sources of cerium and other light rare earths. It is complex compound with rare earth carbonates and fluorides [1]. There are several hydrometallurgical methods for extracting such rare earths from bastnaesite. The sulfuric acid leaching can dissolve almost all of Ce^{4+} , RE^{3+} , F^- and Th^{4+} , so it is considered to be more advanced technology for bastnaesite comprehensive utilization [2, 3]. However, F^- coordinates with Ce^{4+} to form $[CeF_2]^{2+}$ complex in sulfuric acid system because of strong coordination ability of F^- [4-6]. The existence of $[CeF_2]^{2+}$ makes it difficult to separate F^- , Ce^{4+} and RE^{3+} , and brings about the formation of the third phase during extraction separation of rare earths. Therefore, the existence of fluoride restricts the application of sulfuric acid leaching process. The fluoride must be removed from sulfuric acid leaching solution.

The most commonly used methods for fluoride removal are precipitation, adsorption, ion exchange, electrodialysis, etc. Adsorption has been found to be the most important one for easy operation, affordable cost and water quality [7]. To our knowledge, no study has been done on the fluoride removal from fluoride-bearing cerium sulfate solution by adsorbent, so it has certain innovation in this field. Among the adsorption materials, the hydrous zirconium oxide prepared by precipitation has attracted attention as adsorbent due to its large surface area, high adsorption rate, heat and radiation resistance, free from the interference of other ions, insoluble in water and good defluorination effect in lower pH. It can be used for defluorination of groundwater and industrial wastewater [8,9].

In this paper, taking fluoride-bearing cerium sulfate solution as the research object, hydrous zirconium oxide was added into the solution to remove fluoride as adsorbent. It is expected to separate fluoride from cerium and eliminate the influence of fluoride on the extraction separation of rare earths in “sulfuric acid leaching-solvent extraction” process of bastnaesite.

EXPERIMENTAL

All of the reagents used were of analytical reagent grade. The stock solutions of Ce^{4+} and F^- were prepared by dissolving cerium sulfate tetrahydrate and sodium fluoride in dilute sulphuric acid. The F^- concentration was adjusted to 0,01 mol/l, and n_F/n_{Ce} was 2. The acidity was analyzed by titration with a standard NaOH with a mixture of Bromocresol Green and Methyl Red as the indicator, and EDTA-Ca as RE complex. 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.

Nicolet-380 fourier transform infrared spectrometer (Thermo Electron Corporation) was used to detect the chemical structure of the adsorbent. S-3400N scanning electron microscope (Hitachi) with an energy dispersive spectrum(EDS) technique was used to scan electron microscopic(SEM) image and detect the surface atomic composition of the adsorbent. UV-2550 uv-vis spectrophotometer was employed to detect the absorbance of the solution. PXSJ-216 ion meter, PF-1 fluoride ion electrode and saturated calomel electrode(Shanghai Precision Scientific Instrument Co., Ltd.) were used to determine the electric potential of F^- .

All adsorption studies were carried out by mixing 1g adsorbent material with 50 ml of fluoride-bearing cerium sulfate solution. The mixture was agitated in a mechanical shaker for 10 min, then the solution was sepa-

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rated by centrifugation. The concentration of fluoride and cerium was measured. Then, the removal rate η was obtained as following expression:

$$\eta = \frac{C_o - C_e}{C_o} \times 100\%$$

where C_o and C_e (mol/l) are the initial concentrations of fluoride and equilibrium concentration at time t .

RESULTS AND DISCUSSION

The FTIR spectra of hydrous zirconium oxide before and after adsorption are presented in Figure 1. It is seen from Figure 1 that the peaks at 3440 cm^{-1} are due to the stretching modes of O-H bonds in -OH groups indicating presence of water molecules in the material, and the peaks at 1630 cm^{-1} are due to the bending modes of H-O-H bonds. The broad peaks at $460\text{--}500\text{ cm}^{-1}$ are assigned to the Zr-O and O-Zr-O bonds in ZrO_2 [10]. The adsorbent's peak observed at 1353 cm^{-1} [11] is for the bending vibration of Zr-OH groups which decreases significantly after fluoride adsorption. This confirms that fluoride has replaced a substantial fraction of -OH groups bound to zirconium.

Figure 2 shows the surface morphology of hydrous zirconium oxide before and after adsorption. The hydrous zirconium oxide has a significantly rougher surface with lots of uniform pores. Compared with hydrous zirconium oxide, the fluoride-adsorbed adsorbent has smaller particles and less pores. The EDS spectrum of fluoride-adsorbed hydrous zirconium oxide is presented in Figure 3. The corresponding EDS spectrum indicates O, Zr, F elements in fluoride-adsorbed hydrous zirconium oxide. The presence of fluoride reveals that fluoride is successfully adsorbed on hydrous zirconium oxide.

The UV-vis spectra of Ce, F-Ce solutions and F-Ce solution after adsorption are seen in Figure 4. It is found that the maximum absorption peak of Ce solution is around 320 nm . A clear blue shift (from 320 nm to 300 nm) occurs in the UV absorption spectrum of F-Ce solu-

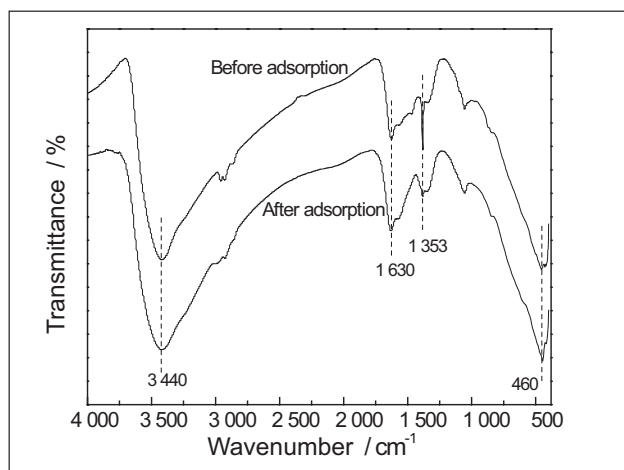


Figure 1 FTIR spectra of hydrous zirconium oxide before and after adsorption

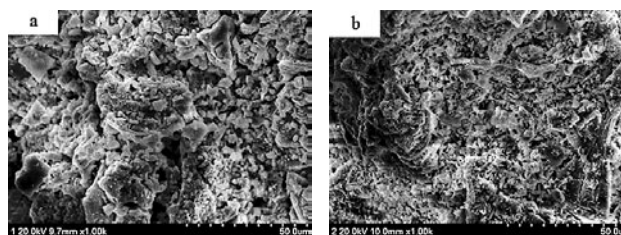


Figure 2 The SEM images of hydrous zirconium oxide before and after adsorption: (a) hydrous zirconium oxide; (b) fluoride-adsorbed hydrous zirconium oxide

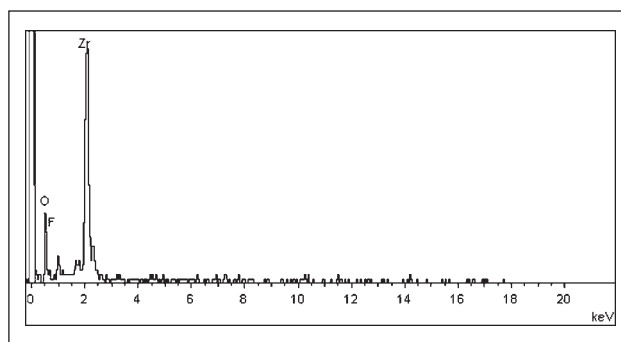


Figure 3 The EDS spectrum of fluoride-adsorbed hydrous zirconium oxide

tion, which is due to that F coordinates with Ce^{4+} to form $[\text{CeF}_2]^{2+}$ complex in sulfuric acid solution. The absorption spectrum of F-Ce solution after adsorption is similar to that of Ce solution with the maximum absorption peak around 320 nm . This is probably because that fluoride is adsorbed by hydrous zirconium oxide and separated from cerium. Cerium exists as Ce^{4+} in solution.

The acidity of fluoride-bearing cerium sulfate solution is an important variable, which influences the complex state of fluoride and cerium, therefore, the effect of acidity on fluoride removal from fluoride-bearing cerium sulfate solution was studied. The obtained results are shown in Figure 5. It is evident from Figure 5 that the high removal rates of fluoride and cerium are got at low acidity. The fluoride removal rate decreases by about 10%, while the cerium removal rate declines sharply with increasing acidity over 0.1 mol/l . With fur-

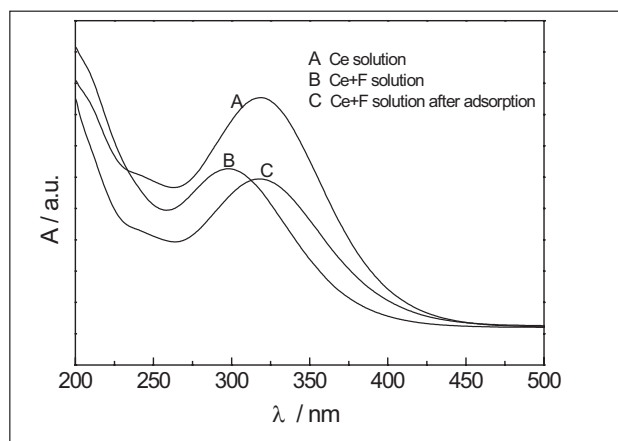


Figure 4 The UV-vis spectra of Ce, F-Ce solutions and F-Ce solution after adsorption

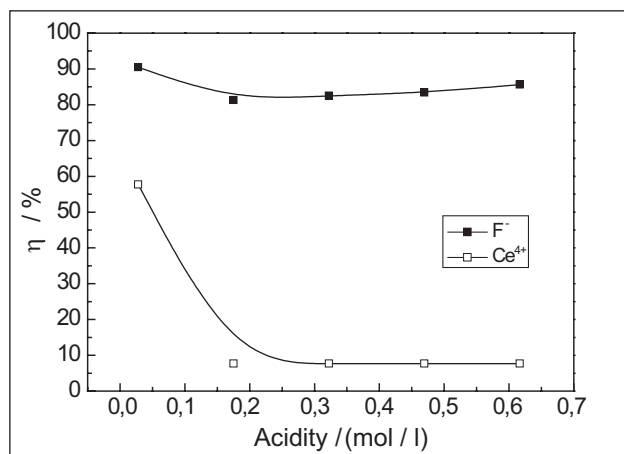
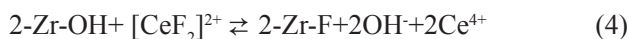
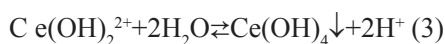
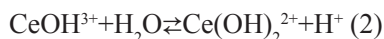


Figure 5 The effect of acidity on removal rate of fluoride and cerium

ther increase in acidity, the fluoride removal rate slightly increases and the cerium removal rate keeps invariable. The results indicate that cerium is not involved in the fluoride adsorption process onto hydrous zirconium oxide under high acidity. The high cerium removal rate at low acidity may be due to the precipitation of hydrous cerium (Eqs.(1)-(3)) [12,13]. Meanwhile, the hydrous cerium shows high uptake of fluoride, so the hydrous zirconium oxide and hydrous cerium both contribute to the high fluoride removal at low acidity. As the acidity increases, the hydrous zirconium oxide can take F⁻ from [CeF₂]²⁺ due to the stronger coordination ability of F⁻ and Zr⁴⁺ compared with F⁻ and Ce⁴⁺. The most probable reactions is given as Eq.(4).



CONCLUSIONS

In this study, amorphous hydrous zirconium oxide was used for fluoride removal from fluoride-bearing cerium sulfate solution. The following findings and conclusions have been drawn:

The FTIR analysis suggests that the adsorption of fluoride onto hydrous zirconium oxide takes place mainly by ion-exchange. The SEM, EDS and UV-vis spectra show that fluoride is successfully adsorbed on

hydrous zirconium oxide, and cerium exists as Ce⁴⁺ in solution.

The cerium is not involved in the fluoride adsorption process under high acidity. The hydrous zirconium oxide can take F⁻ from [CeF₂]²⁺ under high acidity.

The study indicates that it is feasible to separate fluoride and cerium from fluoride-bearing rare earth sulfate solution using hydrous zirconium oxide, and eliminate the influence of fluoride on the extraction separation of rare earths.

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