

Article

Study on Reduction Stripping Kinetics of Ce^{4+} Using a Constant Interfacial Area Cell with Laminar Flow

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Abstract: The reduction stripping kinetics of Ce^{4+} by HEH/EHP was studied by a constant interfacial area cell with laminar flow. The effects of stirring speed, temperature, specific interfacial area, Ce^{4+} concentration in the organic phase, free extractant concentration in the organic phase, HCl concentration, and H_2O_2 concentration on the stripping rate were investigated. The control mode and control steps of stripping process were judged. The kinetic equation of stripping was derived. The mechanism of stripping process was discussed. The results show that the stripping process is controlled by both diffusion and interfacial chemical reaction. The apparent activation energy E_a was calculated using Arrhenius's formula. The kinetic equation of Ce^{4+} reduction stripping is $R = k[\text{Ce}^{4+}]_{(o)}^{1.08}[\text{HEH/EHP}]_{(o)}^{-1.03}[\text{H}^+]_{(a)}^{0.99}[\text{H}_2\text{O}_2]_{(a)}^{0.53}$, and the apparent rate constant k is $10^{-3.66} (\text{mol}^{-0.57} \cdot \text{L}^{0.57})/\text{min}$.



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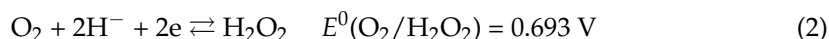
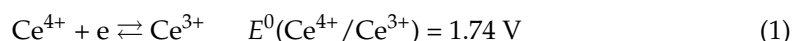
Keywords: cerium; HEH/EHP; reduction stripping; kinetics

1. Introduction

Rare earth elements play an important role in the transformation of traditional industries and the development of emerging industries. They are also an important national nonrenewable strategic resource [1–3]. Cerium (Ce), as the most abundant light, rare earth element in the crust, has played a vital role in a wide range of areas such as catalysis, laser, glass, antioxidants, etc., due to its unique physicochemical properties. Therefore, it is essential to study the recovery and separation of cerium [4]. Solvent extraction known as liquid–liquid extraction is a separation technique in which a metal is transferred from an aqueous phase to another immiscible (or partially miscible) liquid. The extractants are generally too viscous to be used in a practical system. Therefore, they are dissolved in an appropriate solvent to improve their hydrodynamic characteristics for ensuring good contact with the aqueous phase [5]. The solvent extraction process, as the most appropriate commercial technology, is widely used for separating and extracting rare earth elements at home and abroad due to its advantages of high capacity, ease of continuous operation, inexpensive setup, and the possibility of zero waste generation.

Di-(2-ethylhexyl) phosphoric acid (HDEHP) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH/EHP) are commonly used acidic phosphorus extractants for extraction of cerium [6–8]. HDEHP has strong acidity and large extraction capacity; however, it has the problems of difficult stripping, easy emulsification, and high acid consumption. One R-O group in dialkyl phosphoric acid molecule in HEH/EHP is replaced by an R group, which is one alkoxy group less than HDEHP, entailing the introduction of a C-P bond. Due to the weakening of the electronegativity of the ester's oxygen atom in the molecule, the acid ionization constant pK_a value increases, the acidity of HEH/EHP is weaker than HDEHP, and the extraction ability is lower than HDEHP. Therefore, it overcomes the shortcomings of HDEHP [2]. The extraction mechanism of Ce^{4+} by HEH/EHP

have been reported by several researchers. Luo et al. studied the mechanism of synergistic extraction of Ce^{4+} from the sulfuric acid medium by HDEHP and HEH/EHP [9]. Li et al. studied the mechanism of Ce^{4+} extraction from sulfuric acid solution with HEH/EHP extractant [10]. The complex formed by HEH/EHP and Ce^{4+} is very stable, and it is difficult to strip directly with an acid solution. In order to strip Ce^{4+} from organic phase, the reduction stripping method is generally adopted in industrial settings. It is widely known that H_2O_2 is both a strong oxidant and a strong reductant, and its standard potential values are as follows [11,12]:



$$E^0 = E^0(\text{Ce}^{4+}/\text{Ce}^{3+}) - E^0(\text{O}_2/\text{H}_2\text{O}_2) = 1.74 - 0.693 = 1.047 > 0 \quad (3)$$

It can be seen from Equations (1)–(3) that H_2O_2 can reduce Ce^{4+} to Ce^{3+} , and no other metal impurities are introduced in the reduction process. Therefore, H_2O_2 is often selected as a Ce^{4+} reducing agent in the industry. There have been many reports on the reduction stripping of Ce^{4+} [13–15]. In the stripping process, Ce^{4+} in the loaded organic phase is first reduced to Ce^{3+} with a reducing agent, and then, Ce^{3+} is stripped into the aqueous phase with a dilute acid solution.

Extraction kinetics is a very attractive field in the study of solvent extraction. Extraction kinetics research not only provides information useful for optimizing processes, but it is also helpful in clarifying the mass-transfer steps, control mode, and the mechanism of extraction. The main methods used in kinetics study include the constant interfacial cell, single drop, and high-speed stirring. The constant interfacial cell is more suitable for studying kinetics in the laboratory due to its simple operation, simple equipment, and convenient calculation [16]. In recent years, there have been a large number of reports on the extraction kinetics of rare earth elements [17–22]. Yan et al. studied the extraction kinetics of Ce^{4+} with HEH/EHP in fluorine-containing sulfuric acid system by using a constant interfacial cell with laminar flow. The apparent kinetic equation of the extraction process was $R = k[\text{Ce}(\text{HF})(\text{HSO}_4^-)^{3+}]^{1.06}[\text{H}_2\text{A}_2]^{2.07}[\text{H}^+]^{-2.43}$ [23]. Zhao et al. studied the extraction kinetics of Ce^{4+} with HEH/EHP from HNO_3 -HF system using the constant interfacial cell method. The extraction kinetic equation was $R = k[\text{Ce}]B^{0.62}\text{HF}^{-0.58}[\text{NO}_3^-]^{0.57}$ [24]. Liao et al. studied the extraction kinetics of Ce^{4+} with Cynax923 from H_2SO_4 -HF system by the laminar constant interfacial cell method. The extraction kinetics equation was obtained, and the mechanism of extraction process was speculated [25]. However, study on the stripping kinetics of Ce^{4+} has not been reported. The study of stripping kinetics possesses important guiding significance in the selection of stripping agents and stripping conditions and the research of stripping mechanisms. In this paper, using HEH/EHP as the extractant and the HCl - H_2O_2 system as the stripping agent, the stripping kinetics of loaded Ce^{4+} in the organic phase were studied, and the control mode and control steps of the stripping process were judged. The apparent activation energy of the reaction was subsequently calculated, the stripping kinetics equation was deduced, and the mechanism of the stripping process was discussed.

2. Materials and Methods

2.1. Reagents and Instruments

All of the reagents used were of analytical grade. Cerium sulfate ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$), ferrous ammonium sulfate ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$), disodium ethylenediamine tetraacetate ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$), sodium diphenylamine sulfonate ($\text{C}_{12}\text{H}_{10}\text{NSO}_3\text{Na}$), hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$), sulfosalicylic acid ($\text{C}_7\text{H}_6\text{O}_6\text{S} \cdot 2\text{H}_2\text{O}$), hydrogen peroxide (H_2O_2), etc., were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shenyang, China). Hydrochloric acid (HCl) was supplied by Shenyang Laibo Science and Trade Co., Ltd. (Shenyang, China). HEH/EHP and sulfonated kerosene were supplied by Shanghai Laiyashi Chemical Co., Ltd. (Shanghai, China).

The following apparatuses were used: SYC intelligent super constant temperature water tank, DW-3 speed regulating magnetic stirrer (Gongyi Yuhua Instrument Co., Ltd. (Gongyi, China)), and micro sampler (Shanghai Gaoge Industry and Trade Co., Ltd. (Shanghai, China)). The kinetics experiment was conducted through the method of circulating constant interfacial area cell with laminar flow. The interfacial cell was proposed by Zheng et al. [26], which is a new development of Lewis cell. The laminar constant interfacial area cell is rectangular, and the stirring paddles are located at both ends of the cell. The aqueous and organic phases are reversely and independently stirred by two stirring paddles at identical speeds, and the fluid flows reversely under the action of the guide plate. The two phases contact at the interface, and ion exchange and mass transfer occur on the constant and stationary interface. The cell can still keep the interface stable at high speed with acceptable experimental reproducibility. The structure of the device is illustrated in Figure 1.

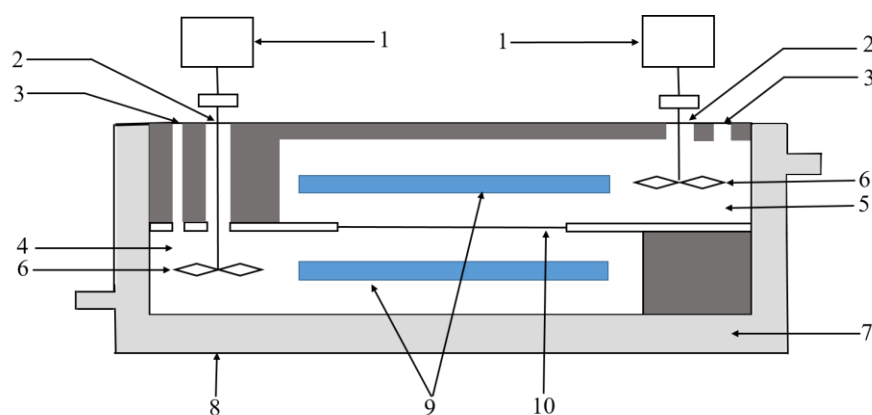


Figure 1. Structure of constant interfacial area cell with laminar flow: (1) agitator; (2) liquid inlet hole; (3) sampling hole; (4) aqueous phase circulation chamber; (5) organic phase circulation chamber; (6) stirring paddle; (7) thermostatic water; (8) thermostatic bath; (9) guide plate; and (10) interface plate.

2.2. Experimental Procedure

In the extraction process, a certain concentration of cerium sulfate solution and HEH/EHP-sulfonated kerosene organic phase was prepared, respectively. A total of 100 mL of cerium sulfate solution and 100 mL of organic phase were subsequently added to a conical flask. The mixture was oscillated at room temperature for 20 min and was then poured into a separating funnel. After phase separation, the raffinate aqueous phase was used to analyze the Ce^{4+} concentration, and the Ce^{4+} concentration in the organic phase was obtained by subtraction.

In the stripping process, the mixed solution of HCl and H_2O_2 with specified concentrations was prepared as the stripping agent. The stripping agent, the Ce^{4+} -loaded organic phase, and laminar constant interfacial area cell should be kept at the experimental temperature in a water bath for 30 min in advance. The stripping agent was injected from the aqueous phase circulation chamber with a syringe. Then, the Ce^{4+} -loaded organic phase was injected from the organic phase circulation chamber to ensure that the final interface was at the interface plate. The ratio of the aqueous phase to the organic phase was 1:1. Through stirring and timing, 0.2 mL solution was taken from the aqueous phase through the sampling hole with a sampler every 10 min. The Ce^{4+} concentration in the aqueous phase was measured, and the Ce^{4+} concentration in the organic phase was obtained by subtraction.

In this experiment, the concentration of Ce^{4+} was determined using $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ titration method in national standard GB/T16484-2009, and the concentration of Ce^{3+} was determined using EDTA titration method in national standard GB/T14635-2008. The acidity of the solution and the concentration of extractant were determined using the NaOH titration method.

2.3. Analytical Method

Assuming that the mass transfer process can be treated as a pseudo-first-order reaction for rare earth ions, the two-phase mass-transfer process of Ce^{4+} can be expressed by the following formula [27]:



where $\text{M}_{(\text{o})}$ represents Ce^{4+} in the organic phase, and $\text{M}_{(\text{a})}$ represents Ce^{4+} in the aqueous phase.

The initial forward reaction rate R_f can be expressed as:

$$R_f = \frac{V}{A} \times \frac{dC_{\text{M(a)}}}{dt} = \frac{1}{Q} \times \frac{dC_{\text{M(a)}}}{dt} = k[\text{M}]^m[\text{N}]^n \dots \quad (5)$$

where $C_{\text{M(a)}}$ is the ion concentration in the aqueous phase, mol/L; V is the phase volume, mL; A is the phase area, cm^2 ; Q is the specific interfacial area, cm^{-1} ; t is the reaction time, min; k is the rate constant; M , N , etc., are the reactants; and m , n , etc., are the reaction orders of the corresponding substance. The volume of the organic phase V is 88 mL. Except for the interfacial area experiment, the two-phase interfacial area A is 23.49 cm^2 .

First, the ion concentration in the aqueous phase was plotted according to the time, and the linear slope was obtained by fitting with the least square method. The initial forward reaction rate R_f under this condition could be subsequently obtained from the slope, and the corresponding rate constant could be obtained by Equation (5).

In the kinetic experiment, the reaction order could be obtained by the isolated variable method. Only the concentration of component M was altered, the experimental conditions and other component concentrations were kept unchanged, and the logarithm of Equation (5) is:

$$\log R_f = m \log[\text{M}] + C \quad (6)$$

where C is a constant, the plot of $\lg R_f$ vs. $\lg[\text{M}]$ was drawn, and the slope of the plot was the reaction order of the corresponding component $[\text{M}]$.

The reverse reaction rate R_r can be expressed as:

$$R_f = \frac{R_f}{D} = \frac{1}{QD} \times \frac{dC_{\text{M(a)}}}{dt} \quad (7)$$

where D is the distribution ratio at reaction equilibrium.

The initial reaction rate R can be expressed as:

$$R = R_f - R_r \quad (8)$$

Since the kinetic experiment was carried out in a state far from equilibrium, the influence of the inverse reaction process on the reaction rate can be ignored, and the initial reaction rate R can be expressed as R_f .

3. Results and Discussion

3.1. Effect of Stirring Speed on Stripping Rate

The stripping process is the mass-transfer process between two phases involving the diffusion of substances at the interface. The effects of diffusion and interfacial chemical reaction on the stripping rate are intricately related to the stripping conditions. Therefore, the investigation of the effects exerted by stirring speed on the stripping rate is conducive to comprehending the kinetic model of the reaction.

The effect of stirring speed on the stripping rate was investigated, and the results are shown in Figure 2. It can be seen that when the stirring speed is in the range of 150–300 r/min, the stripping rate is directly proportional to the stirring rate. This is because the interfacial viscous film is thicker when stirring at low speed, which makes it difficult for substances to diffuse to the interface. In this area, the stripping process should be controlled by diffusion. When the stirring speed is in the range of 300–350 r/min, the

change of stripping rate is small, and the so-called kinetic “plateau” appears, indicating that the diffusion process no longer determines the reaction rate of the stripping process. At this time, there are two possibilities. One is that the interfacial viscous film disappears, and the barrier effect of the interface on mass transfer disappears. The stripping process belongs to interfacial chemical reaction control. The other is that the interfacial viscous film still exists, but the thickness no longer decreases with the increase of stirring speed. The obstruction of the interface to the mass-transfer process becomes a fixed factor, and the stripping process is controlled by the mixing of diffusion and chemical reaction [27]. When the stirring speed exceeds 350 r/min, the stripping rate increases sharply. Combined with the phenomenon of the experimental process, this finding is due to the disturbance caused by the high stirring speed in the two-phase contact interface fluctuation of the constant interfacial area cell.

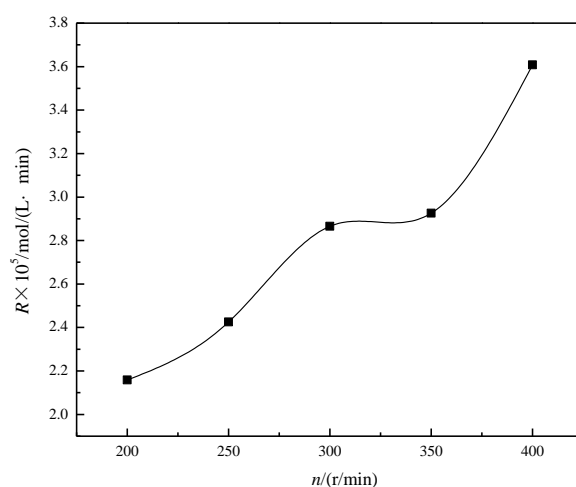


Figure 2. Effect of stirring speed on the stripping rate (experimental conditions: HEH/EHP concentration 0.2 mol/L, Ce^{4+} concentration in organic phase 0.02 mol/L, HCl concentration in stripping agent 6.0 mol/L, $c(\text{H}_2\text{O}_2)_{(a)}:c(\text{Ce})_{(o)}$ 2:1, and temperature 25 °C).

It can be concluded that when the stirring speed is in the range of 300–350 r/min, the stripping process is kinetic control or mixed control of the diffusion and chemical reaction. The study of stripping kinetics mainly delves into the investigation of mass-transfer law under the control of the chemical reaction. To mitigate the influence of diffusion, the stirring speed of subsequent experiments is fixed at 300 r/min while maintaining the stability of the interface.

3.2. Effect of Temperature on Stripping Rate

If the stripping process is controlled by the chemical reaction, the effect of temperature on the stripping rate will be very sensitive. The control step of the stripping process can be judged by the apparent activation energy of the reaction. When the reaction is controlled by diffusion, the activation energy is generally less than 20 kJ/mol; when the reaction is controlled both by diffusion and interfacial chemical reaction, the activation energy is generally between 20 and 42 kJ/mol; when the reaction is controlled by interfacial chemical reaction, the activation energy exceeds 42 kJ/mol [28].

According to Arrhenius’s formula:

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (9)$$

where R is the molar gas constant, t is the absolute temperature, A is the reaction frequency factor, and E is the reaction activation energy.

The logarithm of Equation (9) is:

$$\log k = -\frac{E}{2.303R} \frac{1}{T} + \log A \quad (10)$$

The following formula can be obtained by combining the logarithm of Equation (5) with Equation (10):

$$\log R_f = -\frac{E}{2.303R} \frac{1}{T} + \log A + m \log[M] + n \log[N] + CL = -\frac{E}{2.303R} \frac{1}{T} + K \quad (11)$$

where K is a constant. It can be inferred from the above formula that $\log R_f$ has a linear relationship with $1/T$, and the reaction activation energy can be obtained from the slope of the straight line.

The effect of temperature in the range of 15–45 °C on the stripping rate was investigated, and the results are listed in Figure 3. It can be inferred from Figure 3 that the stripping rate is directly proportional to temperature, indicating that the increase of temperature is conducive to the stripping of cerium. From the slope of the $\log R_f \sim 1/T$ line, the apparent activation energy E_a of the stripping reactions at different stirring speed are calculated to be 18.38 kJ/mol, 22.40 kJ/mol, and 26.23 kJ/mol. Values of E_a have corroborated the results of stirring speed experiments, which confirm the stripping process is controlled by both diffusion and interfacial chemical reaction when the stirring speed is in the range of 300–350 r/min. According to the thermodynamic research conclusion of $E_a > 0$, the stripping of cerium is an endothermic reaction. Increasing the reaction temperature can not only improve the stripping ratio but also improve the stripping rate.

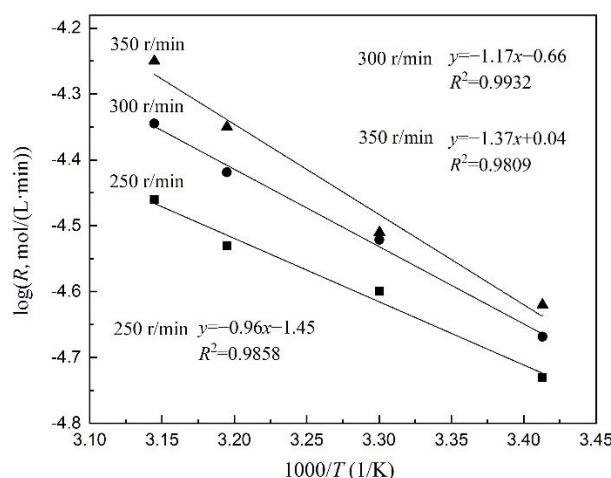


Figure 3. Effect of temperature on the stripping rate (experimental conditions: HEH/EHP concentration 0.2 mol/L, Ce^{4+} concentration in organic phase 0.02 mol/L, HCl concentration in stripping agent 6.0 mol/L, $c(\text{H}_2\text{O}_2)_{(a)}:c(\text{Ce})_{(o)}$ 2:1, and stirring speed 250 r/min, 300 r/min, 350 r/min).

3.3. Effect of Specific Interfacial Area on Stripping Rate

In the stripping process, the chemical reaction controlling the stripping rate may occur in the bulk phase (aqueous phase or organic phase) or the interface. The chemical reaction region can be judged by studying the change of the initial rate of stripping with the ratio of the interfacial area to the volume of the solution containing metal ions (i.e., the specific interfacial area). If the chemical reaction controlling the stripping rate takes place in the bulk phase, the initial rate remains independent of the phase volume and interfacial area. If the chemical reaction takes place in the interface region, the reduction of metal ions concentration per unit time in the bulk phase is directly proportional to the number of molecules crossing the interface per unit time and inversely proportional to the total volume of the aqueous phase. Therefore, the initial rate of the stripping process is directly proportional to the specific interfacial area. The effect of specific interfacial area on

stripping rate was investigated in the range of $0.168\text{--}0.276\text{ cm}^{-1}$. The results are shown in Figure 4. It can be seen that the stripping rate increases with the increase of specific interfacial area and demonstrates a linear relationship, indicating that the chemical reaction in the stripping process takes place in the interface region.

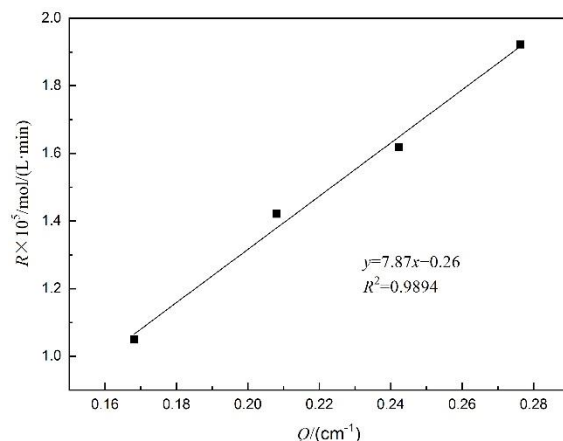


Figure 4. Effect of specific interfacial area on the stripping rate (experimental conditions: HEH/EHP concentration 0.2 mol/L, Ce^{4+} concentration in organic phase 0.02 mol/L, HCl concentration in stripping agent 6.0 mol/L, $c(H_2O_2)_{(a)}:c(Ce)_{(o)}$ 2:1, temperature 25 °C and stirring speed 300 r/min).

3.4. Effect of Ce^{4+} Concentration in Organic Phase on Stripping Rate

The stripping reaction involves the liquid–liquid two-phase mass-transfer process. The order of chemical reactions involving cerium ions can be judged by analyzing the effect of initial loaded Ce^{4+} concentration in the organic phase on stripping rate. The effect of loaded Ce^{4+} concentration in the organic phase on the stripping rate was investigated, and the results are depicted in Figure 5. It can be inferred that the stripping rate is directly proportional to the Ce^{4+} concentration in organic phase. The increase of loaded Ce^{4+} concentration in the organic phase will increase the saturation of Ce^{4+} in the organic phase, thereby impacting the binding force between Ce^{4+} and extractant molecules, which makes the stripping easier. In the experimental concentration range, $\log R_f$ has a linear relationship with $\log[Ce]$, with a linear slope of 1.08. The results show that the stripping of Ce^{4+} in HEH/EHP is a first-order reaction.

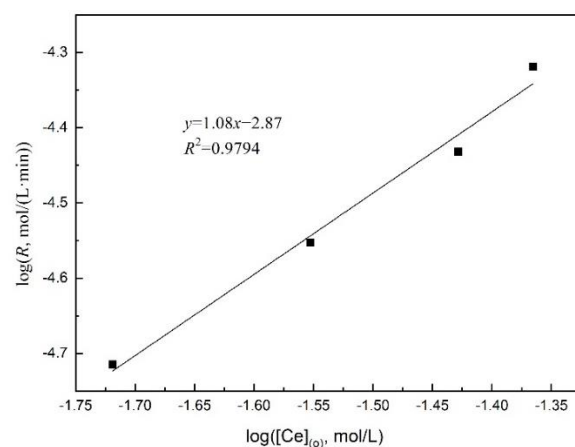


Figure 5. Effect of total cerium concentration in organic phase on the stripping rate (experimental conditions: HEH/EHP concentration 0.1 mol/L, HCl concentration in stripping agent 6.0 mol/L, $c(H_2O_2)_{(a)}:c(Ce)_{(o)}$ 2:1, temperature 25 °C and stirring speed 300 r/min).

3.5. Effect of Free HEH/EHP Concentration in Organic Phase on Stripping Rate

The effect of the concentration of free extractant in the organic phase on the stripping rate was investigated. The results are illustrated in Figure 6.

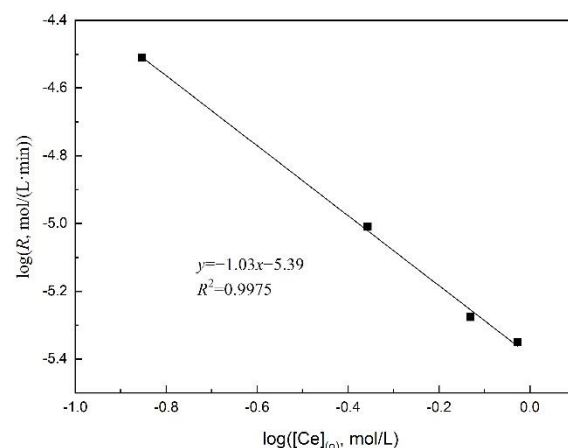


Figure 6. Effect of free extractant concentration in organic phase on the stripping rate (experimental conditions: Ce^{4+} concentration in organic phase 0.02 mol/L, HCl concentration in stripping agent 6.0 mol/L, $c(H_2O_2)_{(a)}:c(Ce)_{(o)}$ 2:1, temperature 25 °C and stirring speed 300 r/min).

From Figure 6, the stripping rate is inversely proportional to the concentration of free extractant in the organic phase. Under the same concentration of Ce^{4+} in the organic phase, the higher the concentration of free extractant in the organic phase, the greater the binding force between Ce^{4+} and extractant molecules, making stripping more difficult. In the range of experimental concentration, $\log R_f$ has a linear relationship with $\log[H_2A_2]$, and the slope of the straight line is -1.03 . The results show a negative first-order relationship towards the concentration of HEH/EHP in the organic phase during the stripping process.

3.6. Effect of H^+ Concentration in Stripping Agent on Stripping Rate

The extraction and stripping of cerium involve an ion-exchange reaction between Ce^{4+} and H^+ . Therefore, the HCl concentration in the stripping agent is an important parameter affecting the stripping rate. The effect of H^+ concentration in the stripping agent on the stripping rate was investigated in the range of 1–6 mol/L. The results are depicted in Figure 7. It can be inferred that the stripping rate increases with the increase of H^+ concentration in the stripping agent. $\log R_f$ has a linear relationship with $\log[H^+]$, and the linear slope is 0.99, showing a first-order relationship towards H^+ in the stripping process.

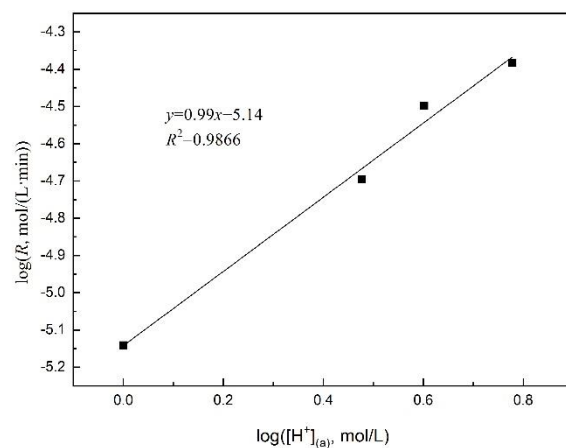


Figure 7. Effect of HCl concentration in stripping agent on the stripping rate (experimental conditions: Ce^{4+} concentration in organic phase 0.02 mol/L, HEH/EHP concentration 0.2 mol/L, $c(H_2O_2)_{(a)}:c(Ce)_{(o)}$ 2:1, temperature 25 °C and stirring speed 300 r/min).

3.7. Effect of H_2O_2 Concentration in Stripping Agent on Stripping Rate

During the stripping process, H_2O_2 will first reduce Ce^{4+} in the loaded organic phase to Ce^{3+} , and Ce^{3+} will subsequently be stripped into the aqueous phase. Therefore, H_2O_2 concentration is another important parameter affecting the stripping rate. The effect of H_2O_2 concentration in the stripping agent on the stripping rate was investigated in the range of 0.01–0.08 mol/L. The results are depicted in Figure 8. It can be inferred that the stripping rate is directly proportional to the H_2O_2 concentration in the stripping agent. $\log R_f$ has a linear relationship with $\log[\text{H}_2\text{O}_2]$, and the linear slope is 0.53. The results show that the reaction order towards H_2O_2 in the stripping process is 0.53.

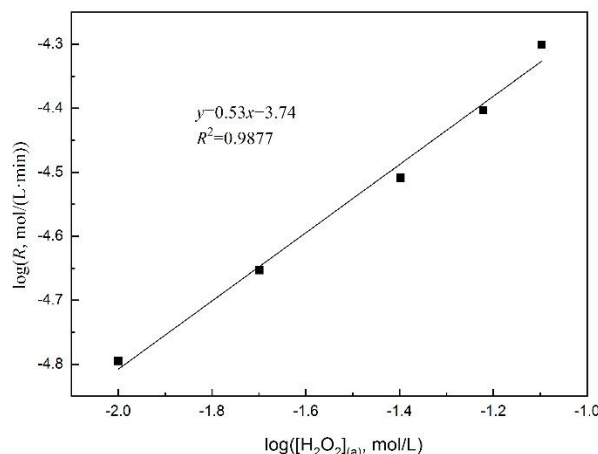


Figure 8. Effect of H_2O_2 concentration in stripping agent on the stripping rate (experimental conditions: HEH/EHP concentration 0.2 mol/L, Ce^{4+} concentration in organic phase 0.02 mol/L, HCl concentration 6 mol/L, temperature 25 °C and stirring speed 300 r/min).

3.8. Derivation of Stripping Rate Equation

According to the law of mass action, the stripping rate can be expressed as:

$$R = k[\text{Ce}]_{(o)}^a [\text{HEH/EHP}]_{(o)}^b [\text{H}^+]_{(a)}^c [\text{H}_2\text{O}_2]_{(a)}^d \quad (12)$$

Taking logarithm on both sides of Equation (12), the following formula can be obtained:

$$\log R = \log k + a \log [\text{Ce}]_{(o)} + b \log [\text{HEH/EHP}]_{(o)} + c \log [\text{H}^+]_{(a)} + d \log [\text{H}_2\text{O}_2]_{(a)} \quad (13)$$

The reaction order (a, b, c, d) of each influencing factor can be deduced through the experiments on the influences of the chemical compositions of the reaction on the stripping rate. From the slopes of the linear relationships between the Ce^{4+} concentration in the organic phase, the free HEH/EHP concentration in the organic phase, the H^+ concentration, and the H_2O_2 concentration in the stripping agent and the stripping rate, the reaction orders of $[\text{Ce}]_{(o)}$, $[\text{HEH/EHP}]_{(o)}$, $[\text{H}^+]_{(a)}$, and $[\text{H}_2\text{O}_2]_{(a)}$ in the reaction equation are 1.08, −1.03, 0.99, and 0.53, respectively. Moreover, according to the intercepts of lines in Figures 4–7, it can be calculated that the $\log k$ is −3.66; thus, the apparent rate constant k is $10^{-3.66} (\text{mol}^{-0.57} \cdot \text{L}^{0.57})/\text{min}$.

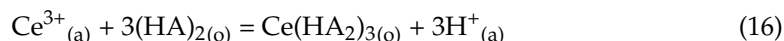
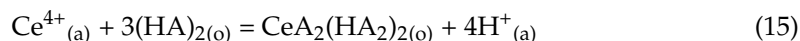
To summarize, the reduction stripping rate equation (apparent kinetic equation) of cerium can be expressed as:

$$R = 10^{-3.66} [\text{Ce}]_{(o)}^{1.08} [\text{HEH/EHP}]_{(o)}^{-1.03} [\text{H}^+]_{(a)}^{0.99} [\text{H}_2\text{O}_2]_{(a)}^{0.53} \quad (14)$$

3.9. The Mechanism of Stripping Process

Numerous studies show that the extraction of rare earth ions by HEH/EHP is a cation-exchange reaction [2,10]. When the concentration of H_2SO_4 is lower than 4.0 mol/L, the slope of $\lg D - \lg[(\text{HA})_2]$ relationship curve of Ce^{4+} extraction by HEH/EHP is 3, and the

slope of $\lg D\text{-}\lg[H^+]$ relationship curve is -4 . Therefore, the mechanism of Ce^{4+} extraction by HEH/EHP is as shown in Equation (15). The mechanism of Ce^{3+} extraction by HEH/EHP under low acidity is shown in Equation (16). In the stripping process, H_2O_2 first reduced Ce^{4+} in the loaded organic phase to Ce^{3+} , and then, the Ce^{3+} was stripped by HCl solution into the aqueous phase. Wang et al. [29] reported that the slope of $\lg D\text{-}\lg[H^+]$ relationship curve of cerium-stripping process is -2.62 , indicating that nearly 3 mol H^+ is required for stripping 1 mol cerium.

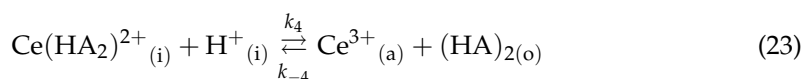
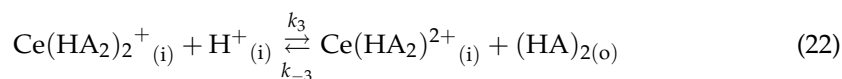
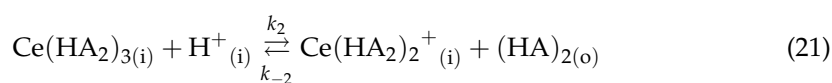
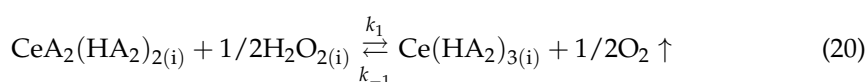
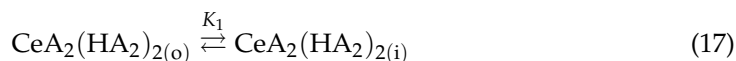


where the HA represents HEH/EHP.

From the above experimental results, it can be concluded that the stripping of cerium in HEH/EHP occurs at the interface, which is a mixed-control mode. The kinetic mass-transfer process from the organic phase to the aqueous phase mainly includes the following steps:

- (1) Ce^{4+} extraction complexes diffused from the organic phase to the reaction zone of the organic phase diffusion layer, and H_2O_2 molecules in the aqueous phase diffused to the interfacial reaction zone;
- (2) Ce^{4+} in the extraction complexes was reduced by H_2O_2 in the reaction zone of the organic phase diffusion layer;
- (3) The generated Ce^{3+} reacted with H^+ diffused to the interface reaction zone through ion exchange;
- (4) The generated $(\text{HA})_2$ diffused from the interface to the organic phase, and the generated Ce^{3+} diffused from the interface to the aqueous phase.

Therefore, it can be speculated that the reduction stripping mechanism of cerium may be [2,10,23]:



where the subscripts “(o)”, “(i)”, and “(a)” represent organic phase, interface, and aqueous phase, respectively. K_1 , K_2 , and K_3 are equilibrium constants; and k_1 , k_2 , k_3 , k_4 and k_{-1} , k_{-2} , k_{-3} , k_{-4} are forward and reverse reaction rate constants, respectively.

Assuming that Equation (22) is the rate control step, that is, the slowest reaction, and at the same time, ignoring the reverse reaction, the stripping rate equation can be obtained as follows:

$$R = k_3[\text{Ce}(\text{HA}_2)_2^+]_{(i)}[\text{H}^+]_{(i)} \quad (24)$$

Due to the speed of the reduction reaction in extraction complexes between Ce^{4+} and H_2O_2 , the Ce^{3+} is difficult to be oxidized to Ce^{4+} by H_2O_2 in the presence of high concentration of Cl^- , and the influence of k_{-1} can be ignored.

The following formulas can be obtained from Equations (20)–(22):

$$-\frac{d[\text{Ce}(\text{HA}_2)_2^+]}{dt} = k_2[\text{Ce}(\text{HA}_2)_3]_{(i)}[\text{H}^+]_{(i)} - k_{-2}[\text{Ce}(\text{HA}_2)_2^+]_{(i)}[(\text{HA})_2]_{(o)} - k_3[\text{Ce}(\text{HA}_2)_2^+]_{(i)}[\text{H}^+]_{(i)} \quad (25)$$

$$\frac{d[\text{Ce}(\text{HA}_2)_3]}{dt} = k_1[\text{CeA}_2(\text{HA}_2)_2]_{(i)}[\text{H}_2\text{O}_2]_{(i)}^{1/2} - k_2[\text{Ce}(\text{HA}_2)_3]_{(i)}[\text{H}^+]_{(i)} \quad (26)$$

Using the steady-state method for treatment, when $-\frac{d[\text{Ce}(\text{HA}_2)_2^+]}{dt} = 0$, $\frac{d[\text{Ce}(\text{HA}_2)_3]}{dt} = 0$ the following formulas can be obtained:

$$[\text{Ce}(\text{HA}_2)_2^+]_{(i)} = \frac{k_2[\text{Ce}(\text{HA}_2)_3]_{(i)}[\text{H}^+]_{(i)}}{k_{-2}[(\text{HA})_2]_{(o)} + k_3[\text{H}^+]_{(i)}} \quad (27)$$

$$[\text{Ce}(\text{HA}_2)_3]_{(i)} = \frac{k_1[\text{CeA}_2(\text{HA}_2)_2]_{(i)}[\text{H}_2\text{O}_2]_{(i)}^{1/2}}{k_2[\text{H}^+]_{(i)}} \quad (28)$$

$$[\text{CeA}_2(\text{HA}_2)_2]_{(i)} = K_1[\text{CeA}_2(\text{HA}_2)_2]_{(o)} \quad (29)$$

$$[\text{H}_2\text{O}_2]_{(i)} = K_2[\text{H}_2\text{O}_2]_{(a)} \quad (30)$$

$$[\text{H}^+]_{(i)} = K_3[\text{H}^+]_{(a)} \quad (31)$$

Substituting Equations (27)–(31) into Equation (24), the following formula can be obtained:

$$R = \frac{k_1 K_1 K_2^{1/2} K_3 [\text{CeA}_2(\text{HA}_2)_2]_{(o)} [\text{H}_2\text{O}_2]_{(o)}^{1/2} [\text{H}^+]_{(a)}}{k_{-2}[(\text{HA})_2]_{(o)} + k_3[\text{H}^+]_{(i)}} \quad (32)$$

Within the scope of experimental research, it is assumed that the mass-transfer process of cerium from the interface to aqueous phase is much faster than that from the aqueous phase to interface, and $k_{-2}[(\text{HA})_2]_{(o)} \gg k_3[\text{H}^+]_{(i)}$; therefore, the stripping rate equation can be expressed as:

$$\begin{aligned} R &= \frac{k_1 K_1 K_2^{1/2} K_3 [\text{CeA}_2(\text{HA}_2)_2]_{(o)} [\text{H}_2\text{O}_2]_{(o)}^{1/2} [\text{H}^+]_{(a)}}{k_{-2}[(\text{HA})_2]_{(o)}} \\ &= \frac{k_1 K_1 K_2^{1/2} K_3}{k_{-2}} [\text{CeA}_2(\text{HA}_2)_2]_{(o)} [\text{H}_2\text{O}_2]_{(o)}^{1/2} [\text{H}^+]_{(a)} [(\text{HA})_2]_{(o)}^{-1} \\ &= k [\text{CeA}_2(\text{HA}_2)_2]_{(o)} [\text{H}_2\text{O}_2]_{(o)}^{1/2} [\text{H}^+]_{(a)} [(\text{HA})_2]_{(o)}^{-1} \end{aligned} \quad (33)$$

where $k = k_1 K_1 K_2^{1/2} K_3 / k_{-2}$.

To summarize, the stripping rate equation derived from rate control step Equation (22) is consistent with the apparent kinetic equation obtained from the experiment, indicating that the stripping process is likely to follow the above steps, and the schematic diagram of mass-transfer process is depicted in Figure 9. The reaction orders of the apparent kinetic equation are non-integer values, which may be due to the non-ideal state of the substances participating in the reaction or existence of other competitive reactions [30].

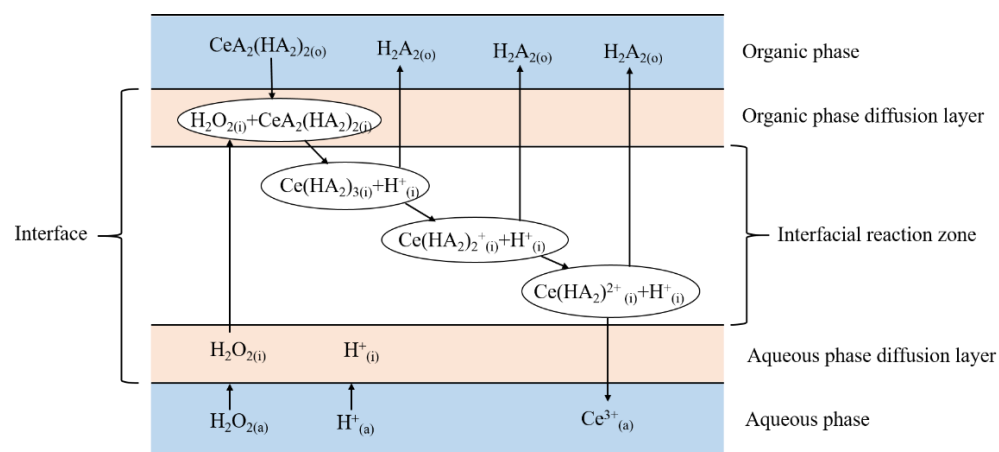
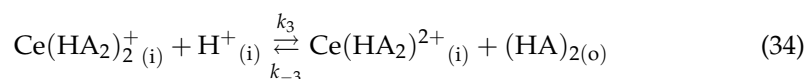


Figure 9. Schematic diagram of mass-transfer process of cerium stripping.

4. Conclusions

The study of stripping kinetics has significant guiding value for the selection of stripping agent and stripping conditions and the research of stripping mechanism. In this paper, the kinetics of reduction stripping of Ce^{4+} in HEH/EHP by $\text{HCl-H}_2\text{O}_2$ was studied by a constant interfacial area cell with laminar flow. The effects of stirring speed, temperature, specific interfacial area, Ce^{4+} concentration in the organic phase, free HEH/EHP concentration in the organic phase, HCl concentration, and H_2O_2 concentration on stripping rate were investigated, and the control mode and control step of the stripping process were judged. The kinetic equation of stripping was deduced, and the mechanism of the stripping process was discussed.

- (1) From the effects of stirring speed, temperature, and specific interfacial area on the stripping rate, the stripping process is controlled by both diffusion and interfacial chemical reaction. The stripping reaction takes place in the interfacial region.
- (2) From the effects of Ce^{4+} concentration in the organic phase, free HEH/EHP concentration in the organic phase, HCl concentration, and H_2O_2 concentration on the stripping rate, the stripping of Ce^{4+} in HEH/EHP is a first-order reaction. It has a negative first-order relationship towards the concentration of HEH/EHP in the organic phase, a first-order relationship towards H^+ , and a reaction order of 0.53 towards H_2O_2 .
- (3) The reduction stripping rate equation of cerium can be deduced as: $R = 10^{-3.66} [\text{Ce}]_{(o)}^{1.08} [\text{HEH/EHP}]_{(o)}^{-1.03} [\text{H}^+]_{(a)}^{0.99} [\text{H}_2\text{O}_2]_{(a)}^{0.53}$, and the apparent rate constant k is $10^{-3.66} (\text{mol}^{-0.57} \cdot \text{L}^{0.57})/\text{min}$.
- (4) It is speculated that the rate control step is as follows:



The stripping rate equation derived by the steady-state method from the rate control step is consistent with the apparent kinetic equation obtained from the experiment.

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