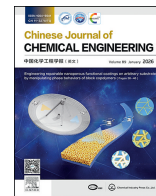




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Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Full Length Article

Bastnaesite carbochlorination process with fluorine fixation agents: An approach for low-waste rare earth extraction



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ARTICLE INFO

Article history:

Received 20 May 2025
Received in revised form
13 August 2025
Accepted 14 August 2025
Available online 1 September 2025

Keywords:

Rare earths
Carbochlorination
Thermodynamics
Separation
Kinetics

ABSTRACT

As an important strategic rare-earth resource, bastnaesite has long been a global research focus. The carbochlorination process, as an efficient and low-cost extraction method, can be applied to treat bastnaesite, achieving ideal rare-earth extraction results in just one-step reaction. By using inexpensive chlorine gas as the chlorinating agent, it avoids lengthy procedural steps and the generation of acid-base waste liquids. Based on this, we propose a novel carbochlorination process for bastnaesite involving a fluorine-fixing agent. Thermodynamic data for the carbochlorination process of bastnaesite were calculated using the group contribution method. Thermodynamic feasibility was verified through Gibbs free energy. The effects of different chlorination times, fluorine-fixing agent dosages, chlorine flow rates, and chlorination temperatures on the carbochlorination process of bastnaesite were investigated. Experimental studies showed that under optimal chlorination conditions, a temperature of 800 °C, a duration of 60 min, a fluorine-fixing agent dosage of 10%, and a chlorine flow rate of 10 L·min⁻¹, the chlorination rates of rare-earth elements, Ca, Ba, and Fe in bastnaesite reached 96%, 99%, 98%, and 99%, respectively. The reaction mechanism was explored and analyzed based on characterization results such as mineral phase composition, micromorphology and thermogravimetry of water-washed residues under different chlorination conditions. Additionally, kinetic experiments were conducted at varying reaction temperatures and chlorine flow rates, revealing that the carbon-chlorination process is primarily controlled by chemical reactions.

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1. Introduction

A group of 17 elements, including lanthanides, scandium, and yttrium, are collectively referred to as rare earth elements (REEs), which can be divided into light rare earth elements (LREEs) and heavy rare earth elements (HREEs) based on their atomic mass [1]. Due to their unique physical and chemical properties, REEs are widely used in aerospace, military, petroleum, functional materials, and other fields [2]. Driven by the new energy revolution, global demand for REEs maintains an annual growth rate of over 5%, with significant increases in advanced applications such as permanent magnets for new energy vehicles, solid oxide fuel cells, and precision ceramics [3]. The application of rare earths in magnetic materials has consistently maintained a high proportion,

and many scholars have conducted in-depth research on this topic. Na *et al.* [4] prepared RE₂Zr₂O₇ (RE = Gd, Dy, Ho, and Er) ceramics as single-phase magnets, which exhibited excellent magnetic properties and low-temperature magnetocaloric effects (MC). Zhang *et al.* [5] developed RENaGeO₄ (RE = Gd, Dy, and Ho) magnetic materials, revealing their structure and magnetic properties, particularly the MC response, through experimental measurements and theoretical calculations. Under relatively low magnetic field variations, the MC parameters of the prepared oxides far exceeded those of the commercial MC material Gd₃Ga₅O₁₂ and surpassed the latest benchmark low-temperature MC materials. Chen *et al.* [6] synthesized Gd₁₁O₁₀(SiO₄)(PO₄)₃ through high-temperature solid-phase reactions. Under a magnetic field change of 0 to 7 T, the material's maximum magnetic entropy change/temperature-averaged magnetic entropy change (5 K-lift) and relative cooling power/refrigerant capacity were 33.76/31.42 J·kg⁻¹·K⁻¹ and 389.98/295.15 J·kg⁻¹, respectively, making it

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suitable for low-temperature magnetic refrigeration applications. However, bottlenecks in rare earth smelting and extraction—particularly the separation challenges caused by complex mineral symbiosis—remain critical obstacles to sustainable industrial development [7].

Bastnaesite, as one of the primary minerals for rare earth extraction, has the advantage of a high total rare earth oxide content of 50% to 80%. However, its strong fluorine coordination structure significantly increases the technical difficulty of efficient and clean extraction. The migration and transformation of fluorine during the smelting process have critical implications for process design and environmental safety. On the process design level, free fluoride ions readily corrode equipment materials, particularly in acidic systems, accelerating the degradation of metal components and necessitating the use of specialized corrosion-resistant materials, which significantly increases capital costs. In terms of environmental risks, fluorides exhibit high toxicity and bioaccumulation potential. If not effectively immobilized and released into water bodies, they can lead to soil acidification, excessive fluoride levels in water, and harm to plant and animal growth as well as human health. Advanced treatment of fluoride pollutants requires complex processes such as precipitation and adsorption, substantially raising waste management costs [8–10]. Therefore, achieving efficient immobilization of fluorine is a core prerequisite for greening and cost reduction in rare earth smelting processes. Current industrial extraction processes mostly rely on multi-step acid-base alternating treatment systems (e.g., sulfuric acid roasting-hydrochloric acid leaching, alkali decomposition, etc.), which can achieve over 90% rare earth leaching efficiency but often suffer from issues such as large fluctuations in wastewater pH and high costs for fluorine pollution control [11–14]. Although the H_2SO_4 roasting system developed by Fu [15] achieved a rare earth leaching rate of over 90%, its fluorine dissolution rate also reached 65%, significantly increasing the difficulty of waste treatment. Liu *et al.* [16,17] innovatively employed an $\text{NaOH}-\text{CaO}-\text{H}_2\text{O}$ system to immobilize fluorine, raising the fluorine mass content in leaching residues to 99.2%, but the 72.5% rare earth recovery efficiency still falls short of industrial demands.

The carbochlorination process, as a simple and efficient treatment method, has garnered attention from researchers in recent years. It enables selective chlorination of diverse and complex mineral systems through Cl_2/C co-activation and achieves graded separation of components by leveraging differences in the melting and boiling points of chlorides [18–20]. This process demonstrates unique application potential in mineral processing due to its outstanding advantages. Firstly, the carbochlorination process utilizes the significant differences in melting and boiling points between various chlorides to achieve separation, avoiding the high-energy consumption of repeated dissolution–precipitation in traditional hydrometallurgy and significantly shortening the process flow. Secondly, this process generates less environmental pollution, as designs such as *in-situ* fluorine fixation enable the harmless treatment of hazardous elements, reducing waste emissions at the source. Additionally, the process has low requirements for raw material grades, offering broad applicability, and can be used for the recovery and utilization of various complex rare earth ores and secondary rare earth resources. Zhang *et al.* [21] developed a carbochlorination technique for rare earth extraction using carbon as a reducing agent, chlorine gas as a chlorinating agent, and SiCl_4 gas as a defluorinating agent, achieving REEs separation *via* chemical transport. However, the silicon tetrafluoride product, being gaseous at room temperature, is difficult to collect, failing to fundamentally resolve the fluorine pollution issue. Based on this, the Special Metallurgy Engineering Research Institute of Northeastern University proposed a novel carbochlorination process for bastnaesite using Al_2O_3 as a fluorine-

fixing agent. This process immobilizes fluorine through *in-situ* formation of $\text{Al}-\text{F}$ complexes, while the generated aluminum chloride concurrently acts as a chlorinating agent, forming an “ $\text{AlCl}_3-\text{Cl}_2$ ” dual-chlorination system to facilitate the reaction [22]. The rare earth chloride (RECl_3) solution obtained from the carbon chlorination process undergoes multi-stage extraction and separation after purification by alkaline earth metal precipitation, yielding a purified RECl_3 solution. The RECl_3 solution is directly used for the preparation of rare earth carbonate *via* cation membrane electrolysis, which is then calcined to produce rare earth oxide (REO). This process establishes a chloride separation and short-flow recycling procedure, significantly reducing the discharge of acidic wastewater throughout the entire process while increasing rare earth chloride efficiency to 96.23%. Currently, thermodynamic research on the chlorination process of bastnaesite still faces the prominent issue of insufficient fundamental data. This study employs the group contribution method to predict thermodynamic parameters for the $\text{RECO}_3\text{F}-\text{Cl}_2-\text{C}$ system [23–26]. Key influencing factors such as chlorination temperature, time, fluorination agent dosage, and chlorine gas flow rate during the reaction were optimized and investigated. The reaction mechanism was explored through characterization analyses such as XRD and SEM-EDS. Additionally, the kinetics and reaction mechanisms of the carbochlorination process under different chlorination temperatures and chlorine gas flow rates were examined. The carbochlorination process demonstrates strong adaptability and can be extended to the clean extraction of other fluorine-containing rare earth minerals (e.g., monazite, xenotime), indicating promising application potential.

2. Experimental

2.1. Materials

The bastnaesite raw material used in the experiment is sourced from Sichuan, China, and its main components and proportions are shown in Table 1. The total proportion of REO in the ore is around 70%, with cerium oxide having the highest content at 34.9%. In addition to REEs, the ore also contains small amounts of alkaline earth metals, iron, sulfur, and other elements. The volatile matter, fixed carbon, and ash content (silicon, iron impurities) of the reducing agent coke account for 9.65%, 67.39%, and 22.96%, respectively. The microstructures of bastnaesite and coke can be observed in Fig. 1. Both bastnaesite and coke consist of irregularly shaped blocks, with the latter's blocks being larger. From the locally magnified images, it can be seen that small particles are attached to the surfaces of both materials, and the edges of the blocks are well-defined. Fig. 2 shows the mineral phase composition of bastnaesite, with the main mineral phase being bastnaesite, along with small amounts of barite, fluorite, calcite, and other mineral phases.

2.2. Experimental methods

The carbochlorination experiment mainly consists of three parts: pelletizing, chlorination roasting, and aqueous leaching (Fig. 3). First, bastnaesite is uniformly mixed with varying proportions of a fluoride-fixing agent (Al_2O_3), 12% reducing agent (coke), and 3% binder (starch), then moistened with distilled water to form

Table 1
Composition and proportion of bastnaesite raw material.

Component	F	SO_3	CeO_2	La_2O_3	Nd_2O_3	SiO_2	CaO	Fe_2O_3	BaO
Proportion/%	3.55	5.36	34.90	26.80	7.00	0.91	4.20	5.46	5.94

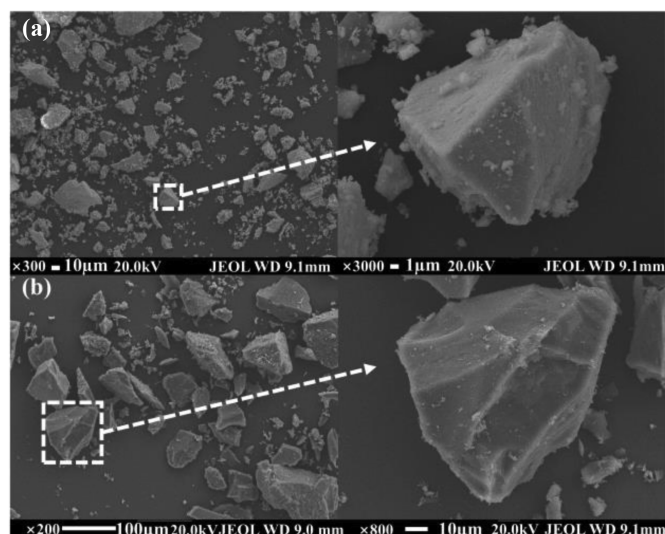


Fig. 1. Microstructures of raw materials: (a) bastnaesite and (b) reducing agent.

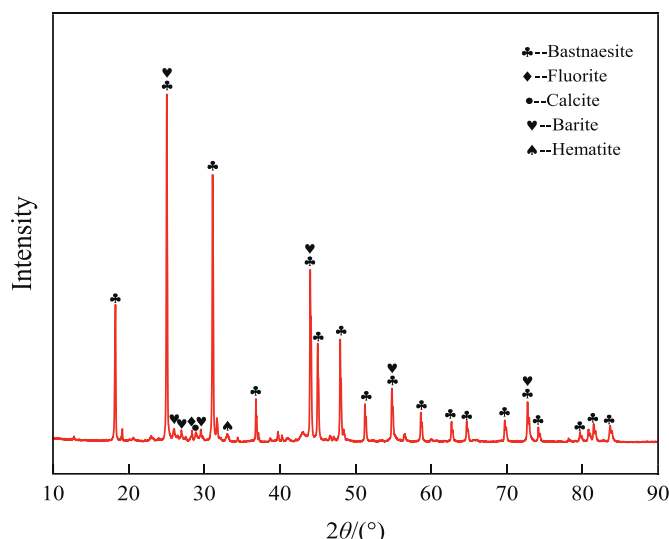


Fig. 2. Mineral compositions of bastnaesite.

pellets. These pellets are dried in an oven at 100 °C and stored for later use [27]. Subsequently, the preformed pellets are placed in a crucible and subjected to chlorination roasting in a chlorination reaction furnace under a chlorine atmosphere. The chlorination reaction furnace is a vertical tube furnace, with a chlorine gas inlet

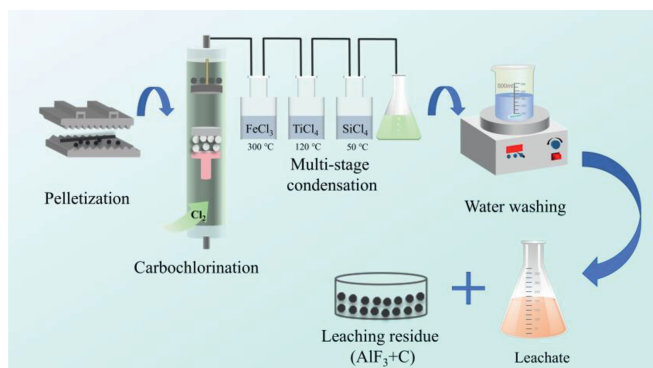


Fig. 3. Process flow in the carbochlorination process of bastnaesite.

device at the bottom and a crucible for loading materials inside to collect solid products. The top of the furnace is equipped with an exhaust device, and the exhaust pipe is connected to a multi-stage condensation system to recover gaseous chlorination products with different melting and boiling points. The products of the carbochlorination process are divided into two types: the first includes FeCl_3 , SiCl_4 , and TiCl_4 , which have relatively low melting and boiling points and volatilize in gaseous form. These can be recovered through the multi-stage condensation system based on differences in their melting and boiling points. The second type includes RECl_3 and alkaline earth metal chlorides (MCl_3), which have higher melting and boiling points and exist in the reaction product as solid molten state. The solid chlorides also contain some unreacted carbon and aluminum fluoride solids, which can be separated by aqueous leaching (80 °C, 30 min). At this stage, the REEs are recovered in the form of RECl_3 in the solution. The chloride solution is then purified, precipitated, and further separated by methods such as extraction to obtain a single RECl_3 solution. Specifically, appropriate amounts of sulfate and carbonate can be sequentially added to the solution to remove calcium and barium impurity ions in the form of barium sulfate and calcium carbonate precipitates, respectively. Subsequently, a multistage countercurrent extraction is performed in the P507–N263 system to ultimately obtain a single RECl_3 solution. The RECl_3 solution can be directly used as raw material for the subsequent cation membrane electrolysis process to prepare REO.

2.3. Characterization methods

To more clearly analyze the reaction products, multiple characterization techniques were employed to comprehensively understand their properties. X-ray fluorescence spectroscopy (XRF, ZSX-Pimus IV, Rigaku, Japan) was used to determine the types and concentrations of elements in the samples. This technique is based on the excitation of characteristic fluorescence in the sample by X-rays, and the elemental composition and content are determined by analyzing the wavelength and intensity of the fluorescence. It is suitable for measuring the elemental composition of solid-phase samples. The elemental composition and content in the liquid phase were tested using a full-spectrum direct-reading inductively coupled plasma emission spectrometer (ICP, Prodigy7 Plus, Teledyne Leeman Labs, USA). This instrument uses plasma as an excitation source to excite elements in the sample, which then emit characteristic spectra. The spectra are analyzed in a full-spectrum direct-reading mode to determine the types and concentrations of elements. The crystal structure and phases of the samples were identified using an X-ray diffractometer (XRD, D8 Advance, Bruker, Germany). The principle involves the diffraction of X-rays by the crystal, where different crystal structures and phases produce unique diffraction patterns. By analyzing these patterns, the crystal structure and phases present in the sample can be determined, which is useful for observing phase transformations during the carbon-chlorination process. The micro-morphology and elemental distribution of the samples were analyzed using a scanning electron microscope (SEM, SU3800, Hitachi, Japan). This instrument scans the sample surface with an electron beam, generating signals such as secondary electrons, which are processed to obtain images of the sample's micro-morphology. Combined with energy-dispersive spectroscopy (EDS), it can determine the elemental distribution across different regions of the sample surface. By integrating the above characterization techniques, the samples were studied from multiple dimensions, including elemental composition, crystal structure, micro-morphology, and elemental distribution. This comprehensive approach provides a thorough understanding of the sample's

composition, structure, morphology, and chemical states, offering a basis for in-depth exploration of reaction mechanisms and optimization of reaction conditions.

2.4. Computational methods

To quantitatively evaluate the chlorination effect on target elements, this study employs the chlorination rate as the key evaluation index, calculated based on the law of mass conservation. The chlorination rate of REEs during the process is determined by the concentration of corresponding chlorides in the aqueous leaching solution and the initial concentration in the raw material, as shown in Eq. (1). The chlorination rates of major non-rare earth elements (non-REEs, e.g., Fe, Ca, Ba) are calculated by analyzing the mass of each element in the raw material and its insoluble residue after chlorination-water washing, as presented in Eq. (2). In the equations, η_1 represents the rare earth chlorination rate, C_1 is the measured concentration in the chloride leaching solution, and V_1 is the constant volume of the chloride leaching solution. C_0 denotes the measured concentration in the raw material digestion solution, and V_0 is the constant volume of the raw material digestion solution. η_2 represents the non-rare earth element chlorination rate, m_0 is the mass of each element in the raw material, and m_1 is the mass of each element in the water-washed residue.

$$\eta_1 = \frac{C_1 V_1}{C_0 V_0} \times 100\% \quad (1)$$

$$\eta_2 = \frac{m_0 - m_1}{m_0} \times 100\% \quad (2)$$

3. Results and Discussion

3.1. Thermodynamic analysis

We selected the Ce element, which accounts for the largest proportion in rare earth minerals, to represent REEs, and provided the possible reaction equations during the carbothermal chlorination process of bastnaesite as shown in Table 2. Firstly, bastnaesite decomposes into REOF and CO_2 at a certain temperature, as shown in reaction 1. As the temperature increases, the carbothermal chlorination reaction of bastnaesite begins to occur under the action of reducing agents and chlorinating agents. In the absence of a fluorine-fixing agent, bastnaesite undergoes carbothermal chlorination to form RECl_3 , REF_3 , and ClF , as shown in reactions 2 to 4. The formation of REF_3 reduces the recovery rate of rare earths, and the generation of ClF can pollute the environment. The chemical reactions occurring with the participation of the fluorine-fixing agent Al_2O_3 are shown in reactions 5 to 7. Alumina reacts to form aluminum chloride in the presence of reducing agents and chlorine gas. Subsequently, Al^{3+} combines with F^- from CeOF and CaF_2 to form AlF_3 , reducing the possibility of forming REF_3 and ClF and avoiding the impact of fluorine on the recovery rate of rare earths. The reactions of calcite and barite in rare earth minerals are shown in reactions 8 and 9, respectively. Bastnaesite also contains non-REEs such as Fe, Ca, Mg, and Si, and the possible reactions they may undergo during the carbothermal chlorination process are shown in reactions 10 to 13.

Due to the lack of thermodynamic data for REFCO_3 and REOF, it is difficult to directly perform thermodynamic calculations for chemical reactions. Mostafa *et al.* [24] first proposed a prediction method for the thermodynamic data of solid inorganic salts, the group contribution method. They used multiple linear regression

Table 2

Possible reactions during the carbochlorination process of bastnaesite.

Possible reactions	Numbers
$\text{CeFCO}_3(\text{s}) = \text{CeOF}(\text{s}) + \text{CO}_2(\text{g})$	1
$\text{CeOF}(\text{s}) + \text{C}(\text{s}) + \text{Cl}_2(\text{g}) = 2/3 \text{CeCl}_3(\text{s,l}) + 1/3 \text{CeF}_3(\text{s}) + \text{CO}(\text{g})$	2
$1/2 \text{CeOF}(\text{s}) + 1/2 \text{C}(\text{s}) + \text{Cl}_2(\text{g}) = 1/2 \text{CeCl}_3(\text{s,l}) + 1/2 \text{ClF}(\text{g}) + 1/2 \text{CO}(\text{g})$	3
$\text{CeOF}(\text{s}) + \text{CO}(\text{g}) + 2\text{Cl}_2(\text{g}) = \text{CeCl}_3(\text{s,l}) + \text{CO}_2(\text{g}) + \text{ClF}(\text{g})$	4
$\text{Al}_2\text{O}_3(\text{s}) + 3\text{C}(\text{s}) + 3\text{Cl}_2(\text{g}) = 2\text{AlCl}_3(\text{g}) + 3\text{CO}(\text{g})$	5
$\text{CeOF}(\text{s}) + 1/3 \text{AlCl}_3(\text{g}) + \text{C}(\text{s}) + \text{Cl}_2(\text{g}) = \text{CeCl}_3(\text{s,l}) + 1/3 \text{AlF}_3(\text{s}) + \text{CO}(\text{g})$	6
$3\text{CaF}_2(\text{s}) + 2\text{AlCl}_3(\text{g}) = 3\text{CaCl}_2(\text{s,l}) + 2\text{AlF}_3(\text{s})$	7
$\text{CaCO}_3(\text{s}) + 2\text{C}(\text{s}) + \text{Cl}_2(\text{g}) = \text{CaCl}_2(\text{s,l}) + 3\text{CO}(\text{g})$	8
$\text{BaSO}_4(\text{s}) + 2\text{C}(\text{s}) + \text{Cl}_2(\text{g}) = \text{BaCl}_2(\text{s,l}) + \text{SO}_2(\text{g}) + 2\text{CO}(\text{g})$	9
$\text{Fe}_2\text{O}_3(\text{s}) + 3\text{C}(\text{s}) + 3\text{Cl}_2(\text{g}) = 2\text{FeCl}_3(\text{g}) + 3\text{CO}(\text{g})$	10
$\text{CaO}(\text{s}) + \text{C}(\text{s}) + \text{Cl}_2(\text{g}) = \text{CaCl}_2(\text{s,l}) + \text{CO}(\text{g})$	11
$\text{MgO}(\text{s}) + \text{C}(\text{s}) + \text{Cl}_2(\text{g}) = \text{MgCl}_2(\text{s,l}) + \text{CO}(\text{g})$	12
$\text{SiO}_2(\text{s}) + 2\text{C}(\text{s}) + 2\text{Cl}_2(\text{g}) = \text{SiCl}_4(\text{g}) + 2\text{CO}(\text{g})$	13

to calculate the contribution values of these ionic groups, and based on these thermodynamic data, the Gibbs free energy change of the reaction can be calculated. Based on this method, we calculated the thermodynamic properties and C_p of REFCO_3 and REOF in bastnaesite, as detailed in Eqs. (3)–(5). Here, n_j is the number of the j -th group, $\Delta_{H,j}$ and $\Delta_{G,j}$ are the contribution values of the j -th group, and Δ_{ij} ($i = a, b, c, d$) are the contribution values of the correlation coefficients.

$$\Delta_f H^\theta = \sum n_j \Delta_{H,j} \quad (3)$$

$$\Delta_f G^\theta = \sum n_j \Delta_{G,j} \quad (4)$$

$$C_p = \sum n_j \Delta_{a,j} + \left(\sum n_j \Delta_{b,j} \times 10^{-3} \right) T + \left(\sum n_j \Delta_{c,j} \times 10^6 \right) / T^2 + \left(\sum n_j \Delta_{d,j} \times 10^{-6} \right) T^2 \quad (5)$$

The chemical reaction equation shown in Eq. (6) can be used to calculate the enthalpy change under standard conditions through Eq. (7). Eqs. (8) and (9) can be used to calculate the enthalpy change at a specific temperature [26]. In the equations, $\Delta_r H^\theta$ represents the standard reaction enthalpy change, ν_B represents the stoichiometric coefficient, $\Delta_f H^\theta(B)$ represents the standard formation enthalpy of the substance, $\Delta_r H^T$ represents the reaction enthalpy change, and C_p represents the constant-pressure heat capacity.

$$aA(\alpha) + bB(\beta) = cC(\gamma) + dD(\delta) \quad (6)$$

$$\Delta_r H^\theta = \sum \nu_B \Delta_f H^\theta(B) \quad (7)$$

$$\Delta_r H^T = \Delta_r H^\theta + \int_{298}^T \Delta C_p dT \quad (8)$$

$$\Delta C_p = \sum \nu_B C_p(B) \quad (9)$$

The relationship between the chemical reaction equilibrium constant (K) and the reaction enthalpy ($\Delta_r H^T$) can be derived from the van 't Hoff equation, as shown in Eq. (10) [28]. According to the definition of the standard equilibrium constant, the Gibbs free energy of the reaction can be calculated using Eq. (11). In the equations, K represents the chemical reaction equilibrium constant, and R is the molar gas constant.

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^T}{RT^2} \quad (10)$$

$$\Delta_r G^T = -RT \ln K \quad (11)$$

To obtain the relationship between Gibbs free energy and temperature, we used the group contribution method to conduct thermodynamic estimations of the reactions involving REEs during the carbochlorination process of bastnaesite. Ce was used to represent the REEs in the ore, while REFeO_3 and REOF in bastnaesite were represented by CeFeCO_3 and CeOF , respectively. CeFeCO_3 can be considered as consisting of Ce^{3+} , F^- , and CO_3^{2-} groups, and CeOF can be regarded as composed of Ce^{3+} , O^{2-} , and F^- groups. Table 3 presents the thermodynamic contributions of these ionic groups, with the values derived from extensive data validation using multiple linear regression by Mostafa *et al.* [24,25]. The thermodynamic data for CeFeCO_3 and CeOF in Table 3 were calculated using Eqs. (3) and (4), while data for other compounds can be found in relevant handbooks [29]. Based on the obtained data, Gibbs free energy was calculated for the chemical reactions of REEs during the carbochlorination of bastnaesite. Linear fitting was applied to the Gibbs free energy–temperature relationship (G–T) reaction equations, and as shown in Table 4, the correlation coefficients R^2 for all reactions were greater than 0.95. Gibbs free energy exhibits a strong linear

Table 3
Thermodynamic contribution of each group.

Group	$\Delta_{H,j}/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{G,j}/\text{kJ}\cdot\text{mol}^{-1}$	$C_p = a + b \times 10^{-3}T + c \times 10^6/T^2 + d \times 10^{-6}T^2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$			
			$\Delta_{a,j}$	$\Delta_{b,j}$	$\Delta_{c,j}$	$\Delta_{d,j}$
Ce^{3+}	−716.558	−569.967	13.011	−7.089	0.762	4.687
CO_3^{2-}	−616.496	−635.99	47.278	86.757	−0.887	−5.133
F^-	−310.918	−326.667	22.041	15.652	−0.244	1.538
O^{2-}	−173.65	−229.836	28.152	12.043	−0.747	−4.023

Table 4
Linear fitting of Gibbs free energy.

Reaction	$\Delta_r G^T/\text{kJ}\cdot\text{mol}^{-1}$	R^2	Temperature/ $^{\circ}\text{C}$
1	$37.957 - 0.1073T$	0.998	—
2	$-177.95 - 0.4018T$	0.997	—
3	$12.776 - 0.2148T$	0.994	—
4	$-93.886 + 0.0087T$	0.997	25–827
	$-72.322 - 0.0236T$	0.999	827–1200
6	$-207.81 - 0.3755T$	0.991	—

relationship with temperature, and the resulting G–T linear equations are presented in Table 4.

To observe the relationship between temperature and Gibbs free energy more intuitively, we plotted G–T diagrams (Fig. 4) for the reactions in Table 2 using the group contribution method and data obtained from Factsage software. Fig. 4 shows that all reactions can proceed forward within the range of 200 $^{\circ}\text{C}$ to 1200 $^{\circ}\text{C}$. From Fig. 4, it can be seen that the Gibbs free energy of the reactions with added fluorine-fixing agents is lower, promoting the reactions. Under these conditions, fluorine tends to form AlF_3 rather than REF_3 or ClF , improving rare earth extraction efficiency while reducing fluorine emissions. The G–T curve of reaction 7 exhibits an inflection point around 1100 $^{\circ}\text{C}$, which is due to phase changes occurring as the temperature reaches the melting or boiling points of the chlorinated products. When the reaction temperature was 800 $^{\circ}\text{C}$, the reaction sequence of the compounds was $\text{CeOF} + \text{AlCl}_3 > \text{CeOF} > \text{Fe}_2\text{O}_3 > \text{Al}_2\text{O}_3 > \text{BaSO}_4 > \text{CaO} > \text{SiO}_2 > \text{MgO} > \text{CaF}_2 > \text{CeFeCO}_3$. This indicates that at this temperature, the carbochlorination reaction of rare earth oxyfluorides was the dominant reaction.

3.2. Carbochlorination experiment of bastnaesite

The study systematically investigated the effects of different chlorination times, fluoride-fixing agent dosage, chlorine flow rate, and chlorination temperature on the carbochlorination reaction of bastnaesite. Reaction time often impacts the efficiency and cost of the process, making it a crucial factor to consider. Under initial reaction conditions of a chlorination temperature of 700 $^{\circ}\text{C}$, fluoride-fixing agent dosage of 10%, and chlorine flow rate of 10 $\text{L}\cdot\text{min}^{-1}$, the chlorination rates of various elements at different reaction times were examined, as shown in Fig. 5(a). Clearly, the rare earth chlorination rate increased with prolonged reaction time. In the initial stage of the reaction (0 to 30 min), the chemical reaction rate was the fastest, and the chlorination rate surged directly to 83%. At this stage, the reaction was dominated by surface activation and decomposition, with rare earth ions released from bastnaesite rapidly reacting with sufficient activated carbon and chlorine on the surface. In the later stage of the reaction (45 to 75 min), the product layer formed during the initial reaction gradually enveloped the unreacted material, hindering chlorine contact and causing the chlorination rate growth to slow. As the product layer thickened, the

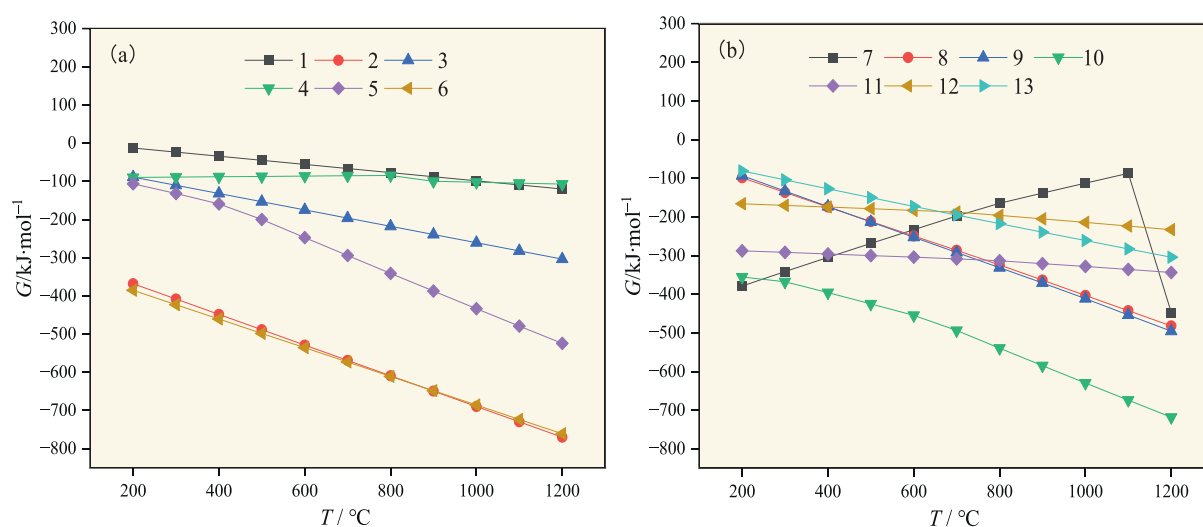


Fig. 4. G–T curves of each reaction equation for the carbochlorination of bastnaesite: (a) REEs, (b) non-REEs.

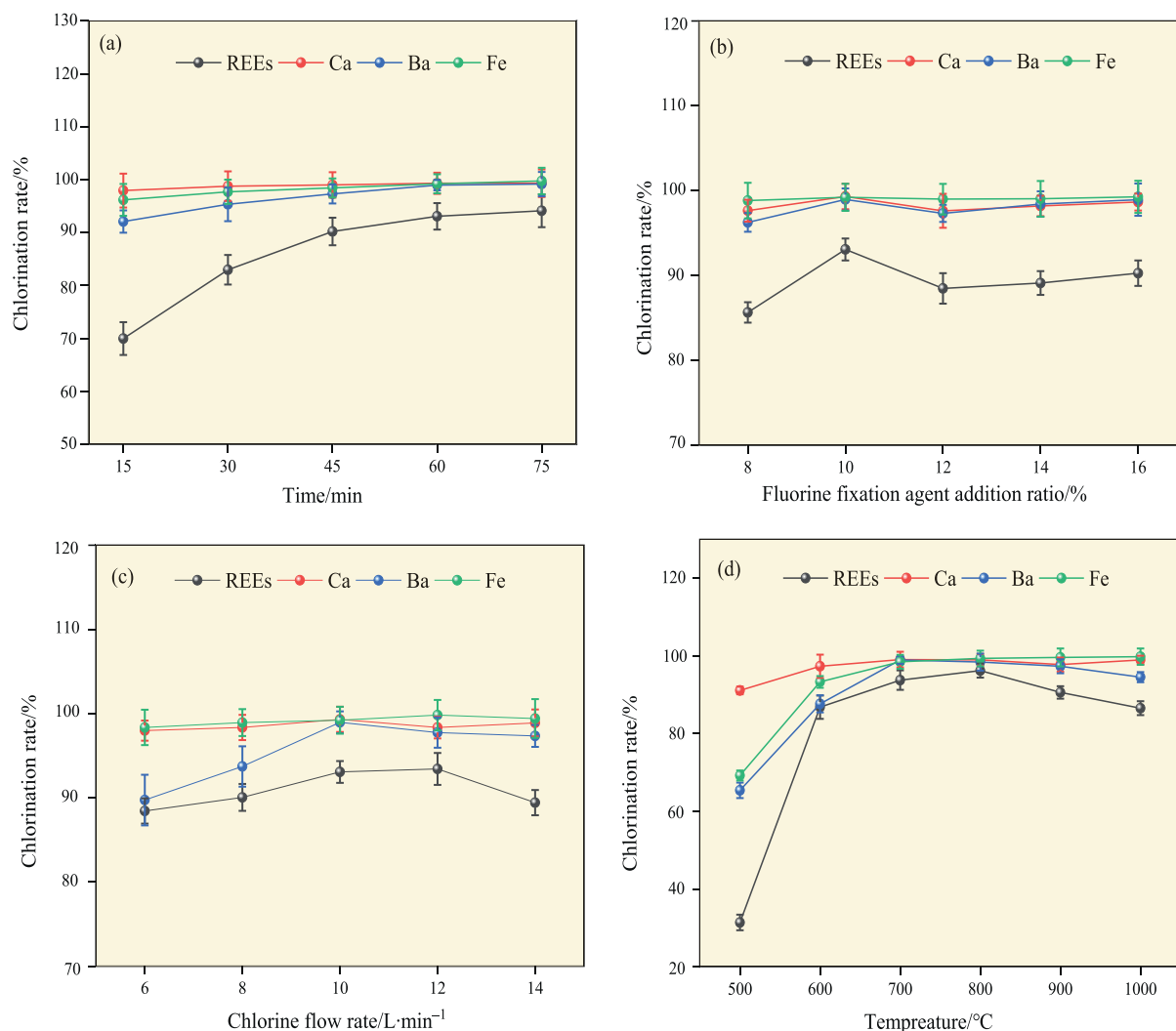


Fig. 5. Chlorination rates of various elements under different chlorination conditions: (a) time, (b) fluoride fixing agent ratio, (c) chlorine flow rate, (d) temperature.

blocking effect became pronounced, and from 60 to 75 min, the rare earth chlorination rate increased by only 1%. Non-REEs such as calcium, barium, and iron achieved chlorination rates of 98%, 92%, and 96% by 15 min, nearly completing the reaction.

Under the initial conditions of a chlorination temperature of 700 °C, chlorination time of 60 min, and chlorine gas flow rate of 10 L·min⁻¹, the effect of different fluoride-fixing agent additions was investigated, as shown in Fig. 5(b). As the fluoride-fixing agent addition increased from 8% to 12%, the rare earth chlorination rate first increased and then decreased. When the fluoride-fixing agent addition increased from 12% to 16%, the rare earth chlorination rate only showed a slight increase. Clearly, either excessive or insufficient addition of the fluoride-fixing agent is unfavorable for rare earth chlorination. Insufficient fluoride-fixing agent prevents fluoride ions from binding with enough aluminum ions, making it impossible to avoid the escape of fluorine. Excessive fluoride-fixing agent overly consumes the carbon source in the pellets, preventing the REEs from reacting completely. When the fluoride-fixing agent addition was 10%, the REEs chlorination rate reached its optimal level, and the fluorine escape rate under this condition was only 13.8%. The fluoride-fixing agent addition had little effect on non-REEs Ca, Ba, and Fe. Regardless of the proportion, the

chlorination reactions of these three elements proceeded thoroughly, with chlorination rates exceeding 97%.

Chlorine gas, as a crucial medium in the carbochlorination process, is one of the key factors to consider in the experiment. The effects of different chlorine gas flow rates (ranging from 6 to 14 L·min⁻¹) on the carbochlorination of bastnaesite at 700 °C were investigated separately, as shown in Fig. 5(c). At lower chlorine flow rates (6 to 8 L·min⁻¹), an adequate chlorine concentration atmosphere could not be provided, preventing sufficient reaction with the material and easily leading to side reactions. When the chlorine flow rate increased to 10 L·min⁻¹, the system had sufficient gas, allowing the bastnaesite pellets to react fully, and the chlorination rates of rare earth and Ba elements increased from 88% to 90%, and from 93% to 99%, respectively. When the chlorine flow rate was too high (12 to 14 L·min⁻¹), the chlorine gas did not have enough time to stay on the pellet surface for reaction, and it also dispersed unreacted material, which was unfavorable for the reaction. The chlorination rates of Ca and Fe elements remained consistently high, exceeding 98%, indicating nearly complete chlorination.

Temperature is a crucial factor affecting the rate of chemical reactions. Fig. 5(d) shows the chlorination rates of major elements

in the carbochlorination of bastnaesite at different temperatures. At a chlorination temperature of 500 °C, the decomposition rate of bastnaesite is slow, with most REEs remaining unreacted, resulting in a rare earth chlorination rate of only 31%. When the chlorination temperature rises above 600 °C, bastnaesite decomposes from REFCO₃ into the more reactive REOF, significantly increasing the rare earth chlorination rate. At 800 °C, the rare earth chlorination rate reaches its optimum at 96.23%. As the reaction temperature further increases to 900 °C to 1000 °C, the rare earth chlorination rate ceases to rise and instead declines. This is partly because the reaction temperature gradually approaches the melting point of RECl₃, causing molten products to encapsulate unreacted solid particles and hinder their contact with chlorine gas. Additionally, high temperatures lead to the volatilization and escape of some chlorides. For the non-rare earth element calcium, a chlorination rate of 91% is already achieved at 500 °C, rising to 99% at 700 °C. Thus, calcium compounds have lower temperature requirements during carbochlorination. As the chlorination temperature increases to 700 °C, the chlorination rate of barium rises from 65% to 94% and remains stable thereafter. Iron forms gaseous ferric chloride during the chlorination process, which enters the exhaust gas treatment system. At 500 °C, the chlorination rate of iron is relatively low at 69%. As the temperature increases to 700 °C, iron almost completely volatilizes as ferric chloride, achieving a chlorination rate of 98%. We conducted component analysis on the leachate under these optimal conditions and found that the main constituents in the leachate include REEs such as La, Ce, Pr, Nd, Sm, and Gd, as well as non-REEs like Ca and Ba. The concentration of rare earth ions in the liquid phase was 25.8 g·L⁻¹, while the impurity ion concentrations of Ba and Ca were 1.1 and 1.9 g·L⁻¹, respectively. No non-REEs such as Fe or Si were detected in the leachate, indicating that their corresponding chlorides had volatilized as gaseous phases during the reaction and would not affect the RECl₃ solution.

3.3. Characterization analysis

The raw material pellets, after undergoing carbochlorination, were washed with deionized water at 80 °C for 30 min, filtered, dried, and then characterized by XRD. The phase composition of the washed residues under different chlorination temperatures and times is shown in Fig. 6. As illustrated in Fig. 6(a), when the chlorination temperature ranged from 500 °C to 600 °C,

bastnaesite decomposed completely, with the main phases being rare earth fluorides, oxyfluorides, and aluminum fluoride. The appearance of aluminum fluoride diffraction peaks indicates that bastnaesite decomposed while simultaneously reacting with alumina to form aluminum fluoride. The disappearance of diffraction peaks for mineral phases such as fluorite and calcite suggests that these byproducts in the rare earth ore had already reacted at this temperature, consistent with the conclusions in Fig. 6(a). At chlorination temperatures of 700 °C to 800 °C, the diffraction peaks of rare earth oxyfluoride phases disappeared, and the products consisted solely of rare earth fluorides and aluminum fluoride, indicating thorough rare earth reactions at this temperature. When the reaction temperature increased to 900 °C to 1000 °C, the diffraction peaks of oxyfluorides reappeared. This was due to the rapid reaction of pellets under high-temperature conditions, resulting in molten or liquid products. The liquid products quickly encapsulated unreacted pellets, leading to residual oxyfluorides and thus reducing the rare earth chlorination rate, which aligns with the results in Fig. 5(d). At a chlorination temperature of 700 °C, the phase composition of the washed residues at different reaction times is shown in Fig. 6(b). It can be observed that the phases in the washed residues were primarily CeF₃, AlF₃, and LaOF. Aluminum fluoride had already formed by the 15-min mark. Before 60 min of reaction, the diffraction peaks of oxyfluorides persisted, indicating incomplete pellet reaction. After 60 min of reaction, the oxyfluoride diffraction peaks disappeared, and the intensity of rare earth fluoride diffraction peaks was the weakest, suggesting a more complete reaction at this stage.

The TG curve of the carbochlorination reaction of bastnaesite obtained for the first time by thermal analysis method, from 100 °C to 1100 °C, is shown in Fig. 7(a), with a heating rate of 15 °C·min⁻¹. Three distinct mass loss steps are clearly observed on the TG curve. The mass loss between 100 °C and 270 °C is attributed to the evaporation of moisture in the pellets. The mass gain from 270 °C to 380 °C results from the reaction of compounds such as calcium and magnesium in the rare earth ore, forming chlorides and increasing the mass. The mass loss between 380 °C and 700 °C is due to the decomposition of bastnaesite in this temperature range, releasing carbon dioxide. The consumption of carbon and the chlorination of alumina also contribute to the mass loss. Since the decomposition process is accompanied by the formation of rare earth chloride products, the mass loss rate is relatively low, reaching only 4.18%. This is the largest mass loss peak in the entire

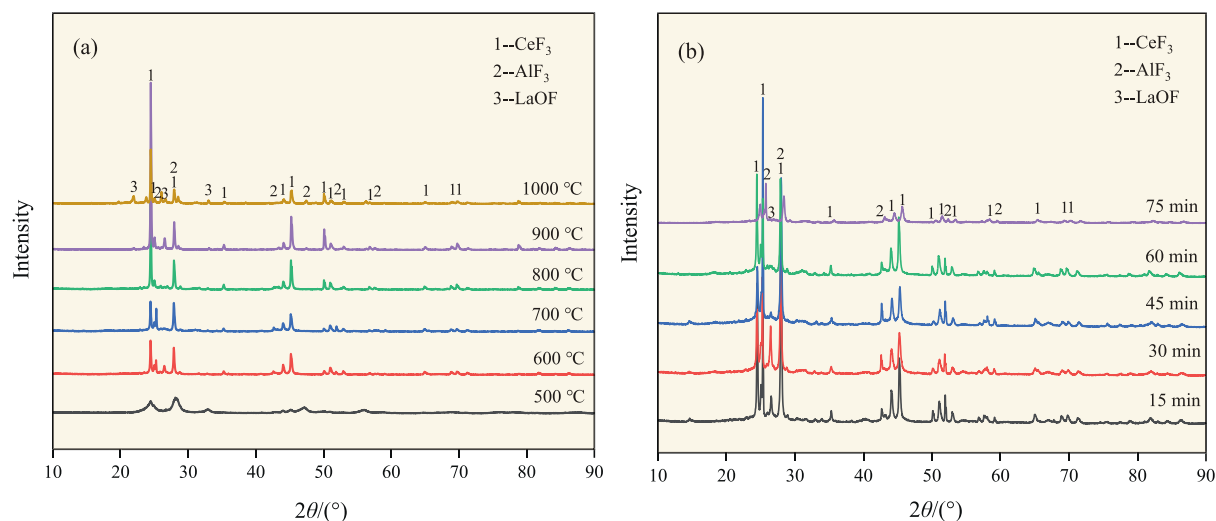


Fig. 6. X-ray diffraction patterns of products under different chlorination conditions: (a) temperature and (b) time.

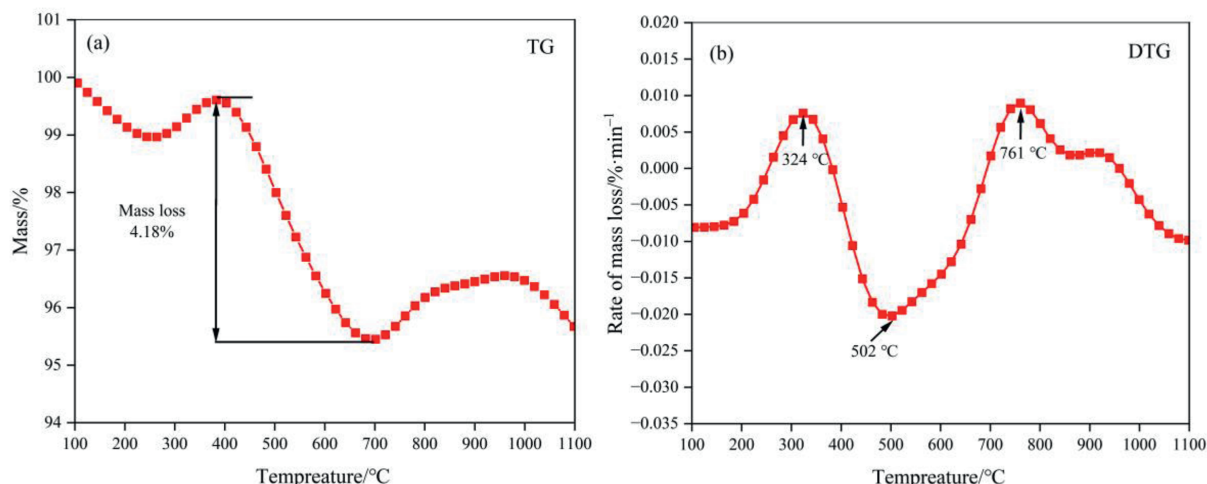


Fig. 7. Thermal analysis curves of the carbochlorination reaction of bastnaesite: (a) TG and (b) DTG.

reaction process. The mass gain from 700 °C to 960 °C occurs as the bastnaesite is fully decomposed, and chloride products begin to form gradually. The mass loss peak between 960 °C and 1000 °C is caused by the volatilization of RECl_3 products at high temperatures, leading to a reduction in mass. To more clearly observe the reaction rates throughout the process, the TG curve was differentiated to obtain the DTG curve shown in Fig. 7(b). Three notable inflection points are observed on the DTG curve. The chlorination reaction of by-products such as calcium and magnesium in bastnaesite reaches its maximum reaction rate at 324 °C. The peak at 502 °C corresponds to the maximum rate of mineral decomposition and reductant consumption reactions. At 761 °C, the chlorination reaction rate of rare earths reaches its fastest, with the rapid formation of RECl_3 products leading to an increase in mass.

The micro-morphology of water-washed residues at different chlorination temperatures (500 °C to 1000 °C) was characterized, and the results are shown in Fig. 8. It can be observed that the overall morphology of the chlorinated residues consists of irregularly shaped blocks, flakes, and fine particles. These irregular blocks are composed of unreacted carbon and decomposed minerals. The flakes are rare earth fluorides gradually formed during the chlorination reaction, while the fine particles consist of unreacted rare earth oxyfluorides and generated aluminum fluoride. As the temperature increases from 500 °C to 800 °C, the blocky phases in the residue gradually transform into flaky phases, and the particles also shift from agglomerated to dispersed forms, surrounding the flakes. This is due to the gradual reaction of rare earth oxyfluorides to form rare earth fluorides and aluminum

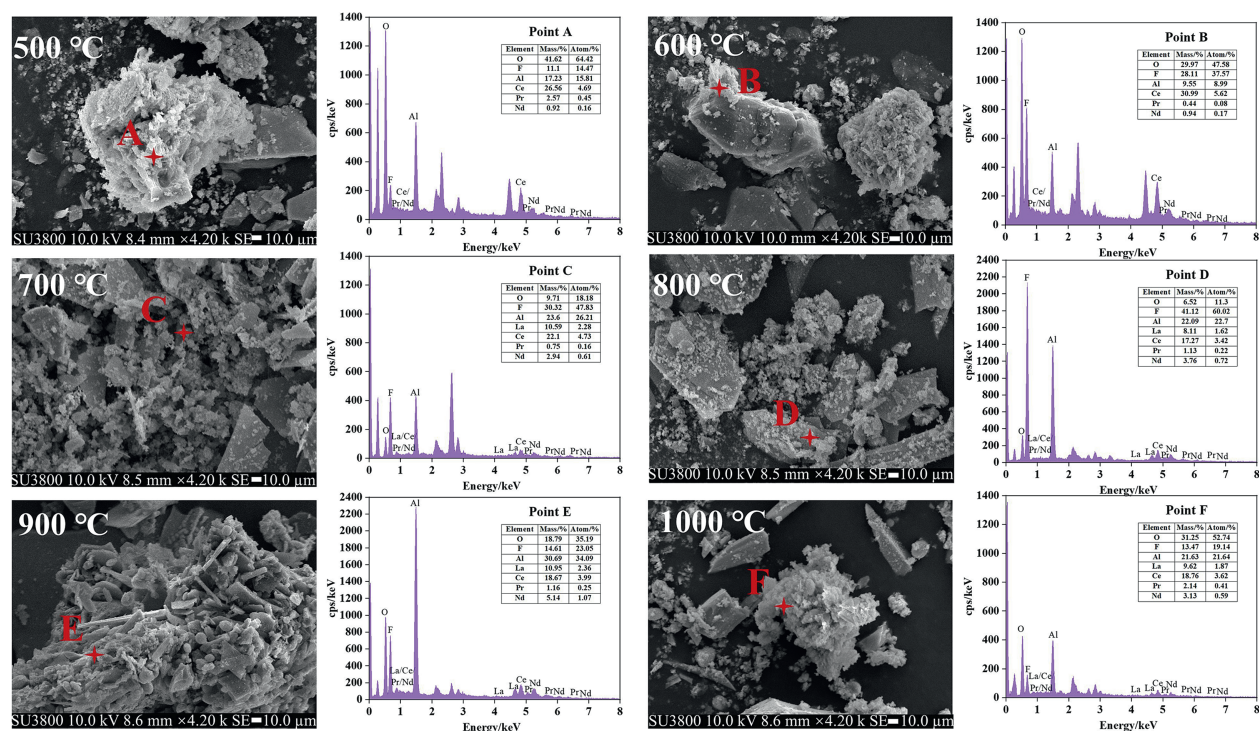


Fig. 8. SEM images of water-washed residues at different chlorination temperatures.

fluoride. When the temperature further rises to 900 °C to 1000 °C, re-agglomeration of flakes and particles occurs. This is because the reaction proceeds rapidly at high temperatures, and the generated rare earth fluorides and aluminum fluoride quickly encapsulate the decomposed minerals, leading to agglomeration. This encapsulation hinders the chlorination reaction of the rare earth fluorides, resulting in a decrease in the chlorination rate of rare earths, which is consistent with the XRD analysis mentioned earlier. EDS point scanning revealed that the water-washed residues mainly consist of O, F, Al, and REEs. As the temperature increases, the oxygen content gradually decreases, while the proportions of fluorine and aluminum increase, indicating the progressive reaction of rare earth oxyfluorides to form rare earth fluorides and aluminum fluoride. At 800 °C, this balance reaches its optimum. However, as the temperature continues to rise, the oxygen content increases again, further confirming the phenomenon of unreacted materials being encapsulated by the product layer on the surface of the pellets.

3.4. Kinetic analysis

The carbochlorination process of bastnaesite involving a fluorine-fixing agent is a gas–solid reaction between solid pellets and gaseous chlorinating agents. In the initial stage of the reaction, a thin layer of chlorination products forms on the outer surface of the pellets. As the reaction progresses, the thickness of the product layer gradually increases, while the solid core gradually shrinks until the reaction is complete, consistent with the characteristics of the unreacted core model. This model is commonly represented by Eqs. (12) and (13), where k is the apparent rate constant of the chemical reaction, t is the chlorination reaction time, and X is the rare earth chlorination rate. When the reaction is controlled by chemical kinetics, its kinetic equation is shown in Eq. (12). When the reaction is controlled by internal diffusion of the products, its kinetic equation is shown in Eq. (13). To investigate the kinetic characteristics of the reaction in detail, carbochlorination experiments were conducted at different reaction temperatures (600 °C to 800 °C) and chlorine flow rates (8 to 12 L·min⁻¹). The extent of rare earth chlorination at different reaction times is shown in Fig. 9. It can be observed that the carbon-chlorination reaction consists of an initial rapid stage (0 to 30 min) and a later slower stage (45 to

75 min). At a chlorination temperature of 800 °C and a chlorine flow rate of 12 L·min⁻¹, the chlorination rates reached 89.59% and 87.16% after 30 min of reaction, respectively. When the reaction proceeded to 75 min, the process slowed significantly, with the rare earth chlorination rate increasing by only about 10%. Fig. 9(a) reveals that temperature has a substantial impact on the carbochlorination process. At 600 °C, the rare earth chlorination rate was 85.82% after 60 min of reaction, whereas at 800 °C, this rate was achieved and surpassed within just 30 min. Fig. 9(b) shows that the influence of chlorine flow rate is relatively pronounced in the initial stages. After 30 min of reaction, the rare earth chlorination rates under chlorine flow rates of 8, 10, and 12 L·min⁻¹ reached 75.39%, 82.97%, and 87.16%, respectively. In the later stages of the reaction, this gap gradually narrowed. After 60 min of reaction, the rare earth chlorination rates for the three conditions reached 91.05%, 93.07%, and 95.63%, respectively.

$$kt = 1 - (1 - X)^{\frac{1}{3}} \quad (12)$$

$$kt = 1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X) \quad (13)$$

From the above analysis, it was found that the carbochlorination reaction of rare earths proceeds in two stages. To reveal the controlling steps of this process, the data from Fig. 9(a) and (b) were fitted into Eqs. (12) and (13), respectively. The results showed a good fit with Eq. (12), and the two-stage fitting results under different chlorination temperatures is shown in Fig. 10(a). The R^2 values in the figures were all greater than 0.91, indicating that the carbochlorination reaction of bastnaesite with the participation of a fluorine-fixing agent is controlled by chemical reactions. To obtain the activation energy and kinetic equations of the chemical reactions, the data from Fig. 9(a) was substituted into the modified Arrhenius equation shown in Eq. (14), and Arrhenius plots were drawn with $\ln k$ as the vertical axis and $1000/T$ as the horizontal axis, as shown in Fig. 10(b). In Eq. (14), A is the pre-exponential factor, R is the ideal gas constant, E_a is the apparent activation energy of the chemical reaction, and T is the reaction temperature. From this, the apparent activation energies for the two-stage chemical reactions under different chlorination temperatures were obtained as 7.83 and 3.79 kJ·mol⁻¹, respectively, with the kinetic equations shown in Eqs. (15) and (16), respectively.

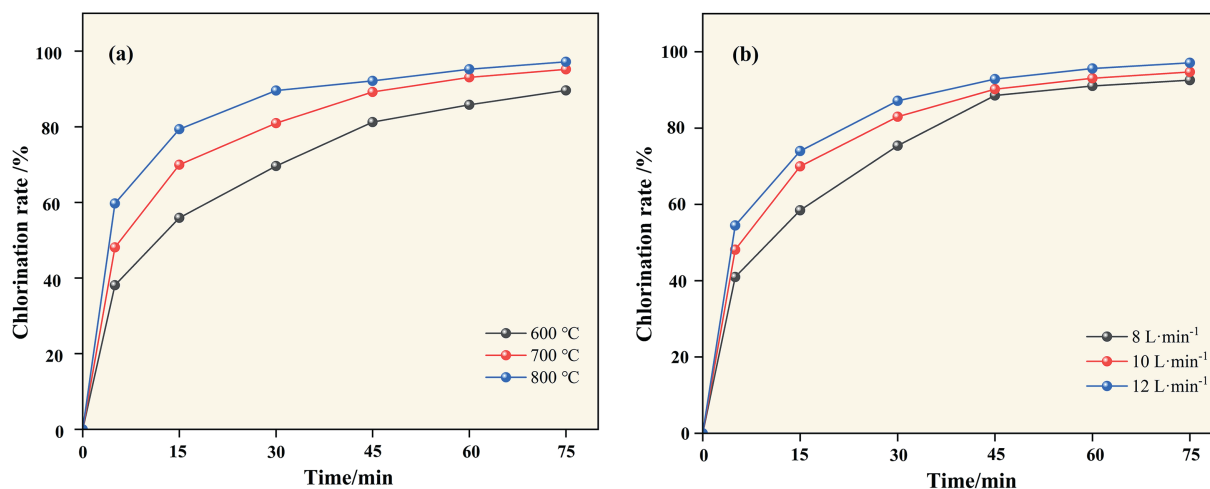


Fig. 9. Rare earth chlorination rates under different reaction conditions: (a) chlorination temperature, (b) chlorine flow rate.

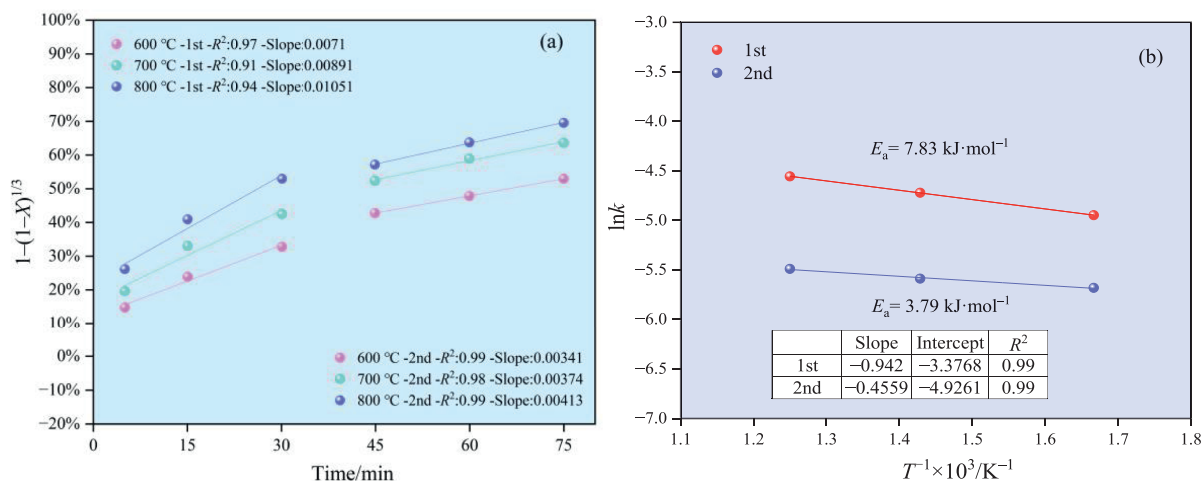


Fig. 10. Kinetic data of carbochlorination reaction: (a) data fitting, (b) Arrhenius.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (14)$$

$$\ln k = -\frac{942.0}{T} - 3.3768 \quad (15)$$

$$\ln k = -\frac{455.9}{T} - 4.9261 \quad (16)$$

3.5. Mechanism discussion

Through in-depth organization and characterization analysis of experimental data, the mechanism of the carbochlorination

reaction of bastnaesite with the participation of a fluorinating agent was elucidated, as shown in Fig. 11 [30]. This reaction can be primarily divided into two key stages: the decomposition stage of bastnaesite and the carbochlorination stage of bastnaesite. During the decomposition stage, under specific reaction conditions, the REFCO_3 phase within the mineral gradually decomposes, releasing carbon dioxide gas and transforming into a more reactive REOF phase. The release of carbon dioxide is of significant importance, as it alters the microstructure of the ore surface, creating additional reactive sites. These newly formed reactive sites increase the contact area between the ore and chlorine gas, thereby facilitating more thorough interaction between the chlorine gas and the ore, creating favorable conditions for the subsequent carbochlorination reaction. Simultaneously, the alumina in the system also undergoes a carbochlorination reaction. Under certain

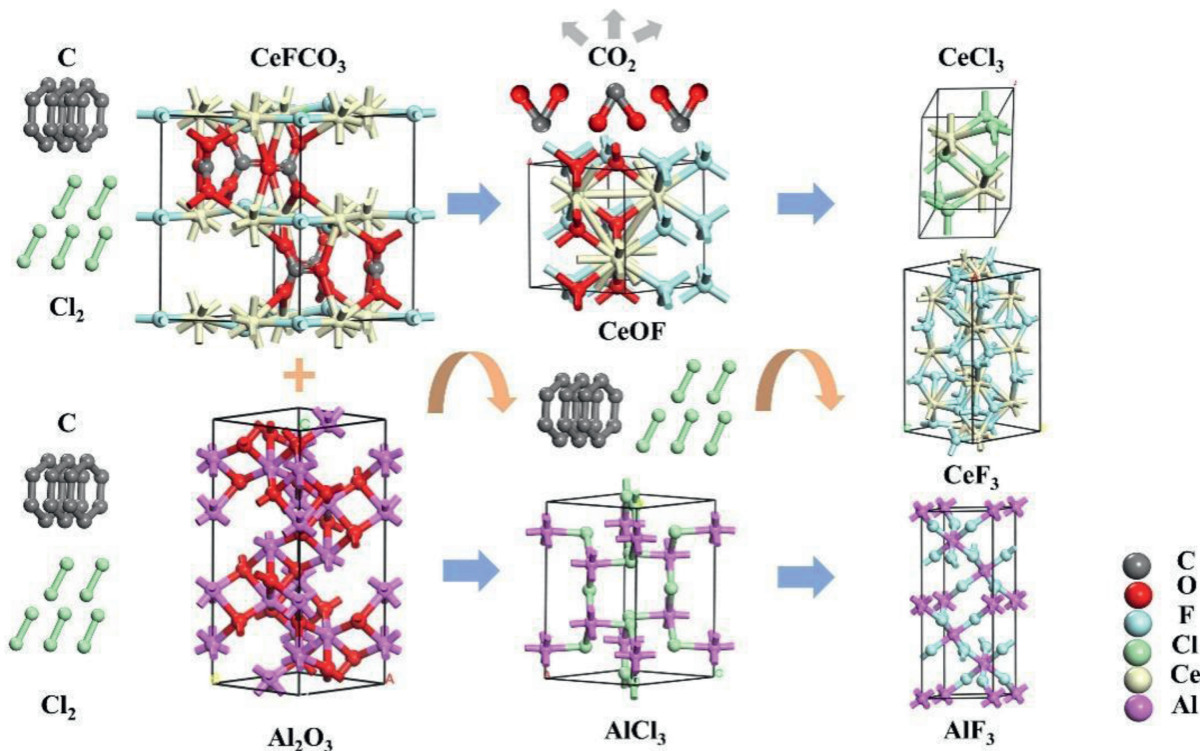


Fig. 11. Mechanism diagram of carbon chlorination of bastnaesite with the participation of a fluoride-fixing agent.

conditions, alumina reacts with carbon and chlorine gas, forming aluminum chloride (AlCl_3). In this process, AlCl_3 plays a dual critical role. On one hand, it acts as a fluoride fixative, effectively immobilizing the fluoride ions generated during the reaction and preventing fluorine loss. On the other hand, it serves as a chloride supplement, providing an ample chlorine source for subsequent reactions with the REOF phase. When AlCl_3 comes into contact with the REOF phase, a chlorination reaction occurs between them. During this reaction, most REEs undergo a transformation from the REOF phase to RECl_3 . Due to unavoidable side reactions or chemical equilibrium factors in the reaction system, only a small portion of REEs form REF_3 . As for aluminum, the entire reaction process completes the transformation from Al_2O_3 to AlCl_3 and then to AlF_3 . This transformation not only reflects the chemical behavior of aluminum in the reaction system but also illustrates the interactions and conversion relationships among various substances in the entire reaction system.

4. Conclusions

This paper conducted a thermodynamic analysis of the carbochlorination reaction of bastnaesite in the presence of alumina using the group contribution method. The effects of different chlorination conditions on the carbochlorination process of bastnaesite were investigated. Combined with the characterization analysis of the washed residue, the reaction mechanism of bastnaesite carbochlorination was proposed, and the following conclusions were drawn.

- (1) Thermodynamic data for the carbochlorination process of bastnaesite were calculated using the group contribution method. The G–T diagram results indicate that all reactions listed in Table 2 can proceed spontaneously within the temperature range of 200 °C to 1200 °C. The addition of a fluorine-fixing agent not only immobilizes fluorine but also promotes the reaction.
- (2) The effects of different fluorine-fixing agent dosages, chlorination temperatures, and chlorination durations on the rare earth chlorination rate were investigated. Both excessive and insufficient amounts of the fluorine-fixing agent lead to a reduction in the rare earth chlorination rate. As the chlorination temperature increased from 500 °C to 800 °C, the rare earth chlorination rate rose from 31% to 96%. Further temperature increases resulted in unreacted pellets being encapsulated by liquid products, hindering the reaction. Additionally, it caused the evaporation of rare earth chlorides, thereby reducing the chlorination rate. The carbochlorination reaction of bastnaesite exhibited the fastest chemical reaction rate during the initial stage (0 to 15 min), achieving a 70% rare earth chlorination rate. In the middle stage (15 to 30 min), the growth trend of the rare earth chlorination rate slowed due to the encapsulation of chlorination products. In the later stage (60 to 75 min), the increasingly thick product layer led to a significant blocking effect. By combining kinetic analysis under different chlorination temperatures and chlorine flow rates, the reaction characteristics of the carbochlorination process of bastnaesite, which is controlled by chemical reactions, were revealed.
- (3) The principles and mechanisms of the carbochlorination process of bastnaesite in the presence of alumina were discussed. The products of this process include gaseous chlorides with low melting and boiling points, solid chlorides with high melting and boiling points, unreacted carbon, and solid residue of AlF_3 . The gaseous chlorides can be recovered through multi-stage condensation based on their

melting and boiling point differences. The solid products can be processed through water leaching, impurity removal, and extraction to obtain single RECl_3 . The carbochlorination reaction of bastnaesite primarily consists of two stages. In the decomposition stage, the mineral phase transforms from REFCO_3 to REOF. In the chlorination stage, REEs transition from REOF to RECl_3 and REF_3 , while aluminum transforms from Al_2O_3 to AlF_3 .

CRediT Authorship Contribution Statement

Haiyue Xue: Writing – original draft. Guozhi Lv: Writing – review & editing. Long Wang: Resources. Jiawei Ren: Investigation. Xinxin Zhao: Investigation. Song Wang: Formal analysis. Tingan Zhang: Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (ZX20230386), the 2023 Special Project for High-Industrial Base Reconstruction Quality Development of the Manufacturing Industry (2023ZY01019-11), the Jiangxi Province “Double Thousand Plan” Project (S2021DQKJ2198), and the sixth batch of top talent support funds (QNBj-2022-04).

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