



Aqueous stability of rare earth and thorium elements during hydrochloric acid leaching of roasted bastnaesite[☆]

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ABSTRACT

In order to study the aqueous stability of rare earth and thorium elements and the reaction mechanism of hydrochloric acid leaching of roasted bastnaesite, E_h -pH diagrams for La-, Nd-, Ce-, Th-(Cl)-(F)-H₂O systems at 20 °C were depicted using HSC Chemistry 6.0 software. E_h -pH diagrams of La-, Ce-, Nd- and Th-Cl-H₂O systems show that trivalent rare earth would be leached into solution by adjusting the acidity of the leaching solution, while tetravalent cerium and thorium would be remained in the leaching residue. And in the case that the pH value of the leaching solution is lower than 2, tetravalent cerium would be partially reduced by chlorine ions (Cl⁻), which is well agreed with the industrial production. It can be inferred from E_h -pH diagrams for the systems La-, Nd-, Ce-, Th-F-H₂O that the leached trivalent rare earth ions (RE³⁺) and tetravalent thorium ions (Th⁴⁺) are preferentially combined with fluorine ions (F⁻) to form sediment during non-reductive acid leaching of roasted bastnaesite. However, when controlling the pH value of the leaching solution below 0, fluorine and tetravalent cerium in the roasted bastnaesite would be leached out in the form of soluble [CeF₃]⁺ complex. That means the precipitation of RE₂F₃ and ThF₄·2.5H₂O can be avoided in the leaching step. According to E_h -pH diagrams for the system Ce-F-Cl-H₂O, [CeF₃]⁺ in the leaching solution would be reduced to CeF₃ precipitate in the presence of Cl⁻, that is to say, tetravalent cerium and fluorine would be firstly leached out to form [CeF₃]⁺, which would then be reduced to CeF₃ precipitate by Cl⁻ in the hydrochloric acid leaching process of roasted bastnaesite.

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1. Introduction

Rare earths (REs) are indispensable strategic materials to develop high-tech and sophisticated national defense technology due to their unique magnetic, optical and electrical properties.¹ Generally in the rare earth industry, bastnaesite, xenotime, ion-absorbed rare earth ore and monazite are used as feed stock to produce rare earth products.^{2,3} Among them, bastnaesite, the main

mineral distributed in Baotou mixed rare earth ore and Sichuan rare earth ore, accounts for the largest proportion of rare earth reserves, as well as the exploitation quantity.

At present, oxidation roasting-hydrochloric acid leaching process is the main process for the treatment of bastnaesite in industrial practise.⁴ In this process, bastnaesite concentrates are first roasted at 500–600 °C to decompose the rare earth fluorocarbonates to rare earth oxyfluorines and rare earth oxides.^{5–9} The roasted bastnaesite is then leached in a hydrochloric acid solution with low concentration to produce first-stage leaching residue and less cerium rare earth chloride solution. The obtained first-stage leaching residue is finally treated by alkaline conversion, water washing, and selective hydrochloric acid dissolution to produce another less-cerium rare earth chloride solution and cerium-rich residue, which can be used for the ferrosilicon alloy production. The less-cerium rare earth chloride solution can be used to produce single rare earth products via solvent extraction. This process is disadvantaged by complicated processes and high acid and alkali

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consumption. More seriously, the associated fluorine would be leached out by water after alkaline conversion, forming fluorine-bearing wastewater, which poses great threaten to the environment. As the Chinese government continues to strengthen the protection of resources and environment, especially “Emission standard of pollutants for rare earths industry” claims the direct emission limit of fluorides (calculated by elemental fluorine) must be less than 8 mg/L for newly established enterprises,¹⁰ the resources and environmental issues of the above process have become more urgent. To deal with the above problems, many researchers have developed improved oxidation roasting processes^{11–20} using additives to fix the fluorine in the slag, to vaporise the fluorine as HF, or to convert the fluorine to soluble salts. Nevertheless, these improved processes are actually unable to replace the conventional process in industrial practise because of their complex processes and inefficient fluorine recovery. Therefore, it is necessary to first investigate the hydrochloric acid leaching process of roasted bastnaesite by thermodynamic calculation.

Potential–pH diagram (E_h –pH diagram) is widely used to describe the relationship between the potential (E_h) of relevant chemical reactions in a particular system and the pH values, and to study the aqueous stability of the elements in the electrolyte solution to further specify the reaction mechanism.²¹ The E_h –pH diagrams for different systems involving rare earths have been widely investigated. Pourbaix²² investigated the E_h –pH diagram of RE–H₂O system and concluded that trivalent rare earth could be separated from tetravalent cerium by adjusting the pH value of the solution. Brookins²³ depicted the E_h –pH diagrams of RE–CO₃^{2–}–H₂O system based on the stable species of rare earth ions in a solution containing CO₃^{2–}. Rare earth ions would react with CO₃^{2–} to form rare earth carbonates precipitate in the pH range of 6–7. Hayes et al.²⁴ improved the E_h –pH diagram of Ce–H₂O system using the stability constants of Ce⁴⁺ and OH[–]. The reactions of Ce(OH)³⁺ → Ce(OH)₂²⁺, Ce(OH)₂²⁺ → Ce(OH)₃⁺, and Ce(OH)₃⁺ → Ce(OH)₄ occurred step by step in an acidic solution as the pH value was gradually increased. Moreover, the changes in the pH value appeared platform period when the pH values were close to 0.75, 1.12 and 1.68, respectively. This is in good accordance with the improved E_h –pH diagram of the Ce–H₂O system. In order to investigate the oxidation of Ce³⁺ by H₂O₂, Yuz and O’Keefe²⁵ depicted the E_h –pH diagrams for the systems Ce³⁺/Ce⁴⁺–H₂O–H₂O₂/O₂. Ce³⁺ could be oxidized to Ce⁴⁺ by H₂O₂ in a pH range of <2, but Ce⁴⁺ could be reduced to Ce³⁺ by H₂O₂ at higher pH values. Kim and Osseo-Asare²⁶ investigated the stable species of La, Ce, Nd and Th elements in the leaching solution during the hydrometallurgical treatment of monazite, and the E_h –pH diagram of Th–, Ce–, La–, Nd–(PO₄^{3–})–(SO₄^{2–})–H₂O systems were finally depicted. Rare earths were precipitated as rare earth phosphate in the solution containing only PO₄^{3–}. However, rare earth sulfate complex was formed in the presence of PO₄^{3–} and SO₄^{2–}, and the stable region of the rare earth sulfate complex could be expanded as the concentration of SO₄^{2–} was increased. This gives a reasonable explanation on the treatment of monazite using sulfuric acid bake and water leaching. Existing studies have been focused on the aqueous stability of rare earths in a solution containing CO₃^{2–}, PO₄^{3–}, and SO₄^{2–}, but little researches has been done on the aqueous stability of rare earths during hydrochloric acid leaching of roasted bastnaesite.

Therefore, thermodynamic calculation on the hydrochloric acid leaching process of roasted bastnaesite has been employed using the E_h –pH diagram module of HSC Chemistry 6.0 software, and the aqueous stability of La, Ce, Nd and Th elements have been investigated to depict the E_h –pH diagrams for the systems La–, Ce–, Nd– and Th–(F)–(Cl)–H₂O, and to further elucidate the reaction

mechanism during hydrochloric acid leaching of roasted bastnaesite. This might provide a theoretical support for the development of a novel efficient, pollution-free process for the treatment of roasted bastnaesite.

2. Thermodynamic data used in E_h –pH diagram

Thermodynamic data used in calculation were taken from the HSC Chemistry 6.0 software database and existing references, as shown in Table 1.

3. Results and discussion

3.1. La–, Ce–, Nd– and Th–Cl–H₂O system

In order to study the stable species of La, Ce, Nd and Th elements in hydrochloric acid medium, the concentrations of metal ions and chloride ion (Cl[–]) were maintained at 1 mol/kg H₂O respectively, and the E_h –pH diagrams of La–, Ce–, Nd– and Th–Cl–H₂O system were depicted, as shown in Fig. 1.

As can be seen in Fig. 1, trivalent rare earth ions (RE³⁺) can stably exist in the solution with a pH value of lower than 6, while Ce⁴⁺ and Th⁴⁺ can stably exist in the solution when the pH value is lower than 0 and 2, respectively, indicating that the separation of RE³⁺ and Ce⁴⁺/Th⁴⁺ can be achieved by adjusting the pH value of the solution, which is well agreed with that of Pourbaix.²⁷ Generally, most of the cerium in roasted bastnaesite exists as tetravalent state. In the following hydrochloric acid leaching step, RE³⁺ can be leached out by adjusting the acidity of the leaching solution, while most of Ce⁴⁺ and Th⁴⁺ remained in the leaching residue, thereby the separation of Ce⁴⁺/Th⁴⁺ and RE³⁺ can be achieved. Moreover, the electrode potential of Cl[–]/Cl₂ ($E(\text{Cl}^-/\text{Cl}_2)$) is lower than that of Ce³⁺/CeO₂ ($E(\text{Ce}^{3+}/\text{CeO}_2)$) as the pH value is lower than 2, indicating that CeO₂ in the roasted bastnaesite can be reduced by hydrochloric acid to form Ce³⁺ and Cl₂. The typical chemical compositions of less-cerium rare earth chloride solution, of which the pH value is around 0.5–1, and roasted bastnaesite in industrial practise are shown in Table 2. It can be seen that above 90% of the cerium is oxidized to tetravalent state after oxidation roasting. The La₂O₃ content is 7 times of the Ce₂O₃ content in the roasted bastnaesite. Above 90% of the La₂O₃ is then leached out in the acid leaching step, but the La₂O₃ concentration in the leaching solution is less than 2.5 times of the Ce₂O₃ concentration. Obviously, Ce⁴⁺ in the roasted bastnaesite was partially reduced to Ce³⁺ during acid leaching, which is consistent with the above analysis.

3.2. La–, Ce–, Nd– and Th–F–H₂O system

In order to study the stable species of La, Ce, Nd and Th elements in the system of fluorine-bearing and non-reductive medium, the concentrations of metal ions and fluorine ion (F[–]) were maintained at 1 mol/kg H₂O, and the E_h –pH diagrams of La–, Ce–, Nd– and Th–F–H₂O system were depicted in Fig. 2. It shows that in fluorine-bearing and non-reductive solution, trivalent rare earth and thorium mainly exist in the form of REF₃ and ThF₄·2.5H₂O, respectively. RE³⁺ and Th⁴⁺ could not stably exist in the fluorine-bearing solution. In addition, the stable regions of RE(OH)₃ and ThO₂ are significantly reduced compared to those of La–, Nd– and Th–Cl–H₂O system. It can be inferred that in fluorine-bearing and non-reductive solution, rare earth fluorine and thorium fluorine are more stable than rare earth hydroxide and thorium oxide under weak alkaline, near neutral or acidic conditions.

Since the coordination reaction between Ce⁴⁺ and F[–] is not systematically considered in Fig. 2, a stable region of soluble

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