



An electrochemical process for the separation of cerium from rare earths

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Received 26 April 2004; received in revised form 12 October 2004; accepted 14 October 2004

Abstract

An electrochemical route to this oxidative precipitation was studied wherein a rare earth chloride solution is subjected to electrolysis enabling the separation of cerium as ceric hydroxide. A rotating cathode was used to avoid formation of hydroxide scale on the cathode surface. The electrolytic and solution parameters were optimized in laboratory scale and bench scale cells. The process occurred at a current efficiency of 60% with an energy consumption of 3.5 kWh/kg of CeO₂. The purity of the product was >95%.

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Keywords: Cerium; Electrochemical oxidation; Rare earths separation

1. Introduction

Due to its specific functional applications, cerium is the most important element of the rare earths. Conventionally, cerium is separated as Ce(IV) hydroxide by oxidative precipitation with sodium hypochlorite after the thorium hydroxide separation stage. Electrolytic separation of cerium hydroxide from mixed nitrate (Dennis and Lemon, 1915) and

chloride (Dennis and Van Den Meulen, 1915) solutions have been reported in the past where the rare earths were separated, making use of the difference in their hydrolysis efficiencies and variations in the pH values required for precipitation. Electrolytic oxidation of cerium and precipitation of ceric phosphate was found to be an easy method for the separation of cerium from the rare earths (Neckers and Kremers, 1928). An electro-oxidation extraction of cerium in TBP-HNO₃ two-phase system was described in which Ce(III) was directly oxidized to Ce(IV) at a platinum anode with simultaneous extraction (Hoh et al., 1988). Recently, simultaneous separation and purification of Eu(III) and Ce(III) was attempted in a diaphragm cell

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(Wang, 1989). In spite of these R and D efforts, the oxidation process with hypochlorite is preferred because of the fast kinetics and high efficiency of oxidation of hypochlorite.

Indirect electrochemical oxidation with in situ generated hypochlorite has been found to be a most convenient method for the conversion of Cr(III) to Cr(VI) and extraction from chromium-containing solid phases (Pushpavanam et al., 2000). Hence, the oxidative precipitation of cerium from mixed rare earth chlorides with in situ generated hypochlorite (from the chloride present in the electrolyte) is studied and reported in this work. The novelty of the above process is avoiding the

transport/storage of chlorine and the low value by-product (NaCl).

Apart from the above, the electrolysis of solutions containing metallic ions that precipitates hydroxides is difficult since a coating of a metallic hydroxide forms on the cathode and hinders the electrolytic process. This has been observed in alkaline metal chloride electrolysis and was overcome by employing a rotating cathode (Vasudevan et al., 1992a,b). This technique has been adopted in this study so that it is easy to switch over to the electrochemical route from the existing conventional chemical oxidation and separation process. The effect of various parameters like electrolyte concentration, pH, cathode current

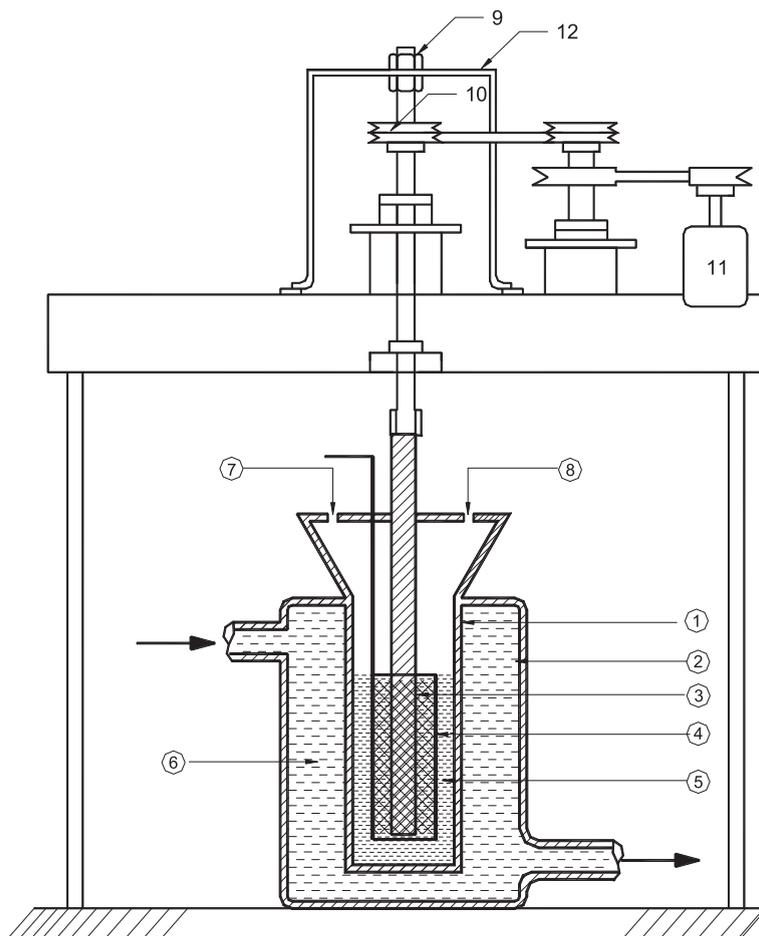


Fig. 1. Laboratory scale cell assembly. (1) cell, (2) thermostat, (3) stainless steel cathode, (4) anode, (5) electrolyte, (6) thermostatic water, (7) and (8) holes to introduce pH sensor and thermometer, (9) mercury cup, (10) pulleys, (11) 0.5-hp motor and (12) copper bus bar.

Table 1
Composition of the rare earth chloride

Analysis	
Rare earth oxides (ReO)	45–47%
CeO ₂ /ReO	45% min.
Sodium as Na ₂ O	1% max.
Calcium as CaO	1% max.
Magnesium as MgO	1% max.
Iron	0.005% max
Lead	10 ppm
Phosphorous as P ₂ O ₅	0.01% max.
Sulphur as SO ₃	0.05% max
Copper, strontium and nickel	Nil
Distribution of rare earths	
CeO ₂ /REO	45–47%
La ₂ O ₃ /REO	22–24%
Nd ₂ O ₃ /REO	19–22%
Pr ₆ O ₁₁ /REO	2–3%
Yttrium and other heavy rare earths	0.5–1.0%

density and rotation speed were optimized in a laboratory scale (1.5A) cell, as well as in a larger 15A cell.

2. Experimental

The electrochemical cell (Fig. 1) consisted of a 0.5-L glass vessel fitted with a PVC cover having suitable holes to introduce the electrodes, a pH sensor and a thermometer. The cathode was a cylindrical

stainless steel (SS304) rod of dimension 0.015 m (dia)×0.07 m (h) fitted to a rotating assembly and positioned at the centre of the cell. A metal anode made of titanium mesh [0.04 m (dia)×0.12 m (h)] coated with RuO₂/TiO₂/SnO₂ based mixed oxides of suitable composition was used (Pushpavanam et al., 1988) and was placed at an interelectrode distance of 1 cm from a centrally positioned cathode. The temperature of the electrolyte was controlled to the desired value with a variation of ±1 °C by adjusting the rate of flow of thermostatically controlled water through an external glass cooling spiral.

Electrical connection to the cathode was through mercury contained in a cup attached to the top end of the rotating shaft driven by a 0.5-hp motor. Regulated direct current was supplied from a rectifier [Aplab, Model L3220-S (20A, 15V)].

The mixed rare earth chloride used in this study was supplied by Indian Rare Earths, Udyogamandal, India. The composition of the rare earth chloride and the distribution of the different rare earths in the mixed chloride are shown in Table 1; Narayanan, 1995); and the same was used for the electrolyte. The electrolyte was prepared using distilled water for the required concentration, 0.45 L of which was used for each experiment. The experiments were run for 6 h at an anode current density of 500 A/m². Current efficiency and purity of the product were monitored as a function of experimental variations, such as concentration of cerous chloride, pH, cathode current

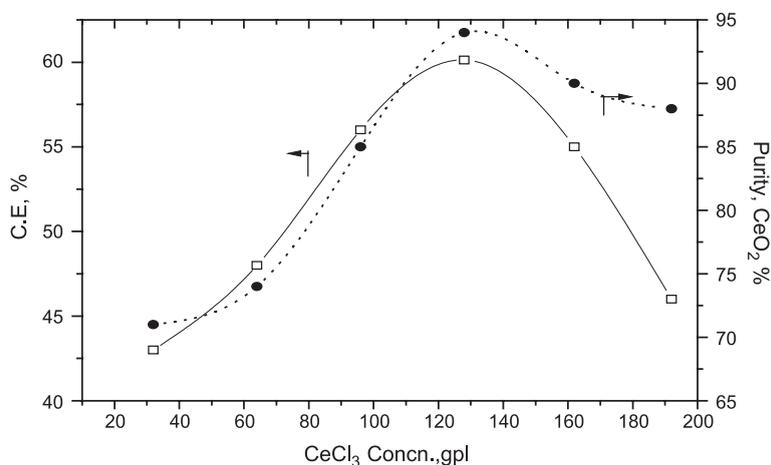


Fig. 2. Variation of current efficiency and purity of CeO₂ with concentration of CeCl₃. Conditions: electrolyte, pH 6.5; temperature, 30 °C; anode current density, 500 A/m²; cathode current density, 300 A/m²; cathode rotation (peripheral velocity), 1.33 m/s.

density and cathode rotation. The concentration of cerium and chloride was estimated with standard analytical procedures (Vogel, 1961).

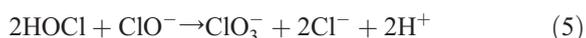
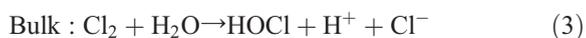
3. Results and discussion

Fig. 2 shows the effect of cerous chloride concentration on the current efficiency and purity of ceric oxide. The current efficiency attains a maximum at about 130 g/L of chloride concentration. Higher concentrations than this results in the formation of an oxide layer on the cathode, hindering further electrolysis. The cell voltage increases due to this layer. The temperature of the electrolyte also increases, which necessitates effective cooling. Otherwise, the rise in temperature may lead to the formation of chlorate or loss of chlorine depending on the operating pH. At lower chloride concentrations, oxygen evolution at the anode must be responsible for the lower efficiency (Vasudevan et al., 1992a). The purity of the product also is higher when the cerous chloride concentration is between 130 and 140 g/L.

The product obtained at higher chloride concentration had to be scraped from the cathode surface and is of lower purity due to Ce(III) hydroxide formed by the reduction of Ce(IV) hydroxide. At lower concentrations, it is probable that Ce(III) hydroxide itself gets

precipitated with the product. But lower concentrations can lead to high cell voltages.

The pH of the electrolyte plays an important role in determining the efficiency, as can be seen from Fig. 3. The reactions occurring during the electrolysis of a chloride solution are shown below:



Reactions (3)–(5) are dependent on the relative concentrations, pH and temperature. Reaction (5) is most favoured under weakly acid and high-temperature conditions. It is seen from the Fig. 3 that both the purity and the current efficiency are high between pH values of 6.0 and 6.5. At pH values lower than 5, the dissociation of hypochlorous acid [reaction (4)] takes place at a lower rate. Although Ce(III) may get oxidized by hypochlorous acid, it exists as Ce(IV) without precipitation. At this stage, the redox system Ce(IV)/Ce(III) may oxidize chloride to chlorine, thus reducing the efficiency.

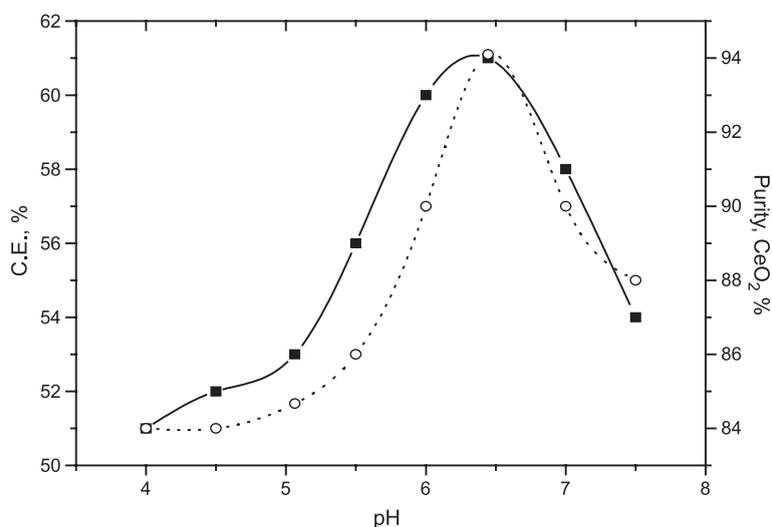


Fig. 3. Variation of current efficiency and purity of CeO₂ with pH of electrolyte. Conditions: electrolyte concentration, 130 g/L; temperature, 30 °C; anode current density, 500 A/m²; cathode current density, 300 A/m²; cathode rotation (peripheral velocity), 1.33 m/s.

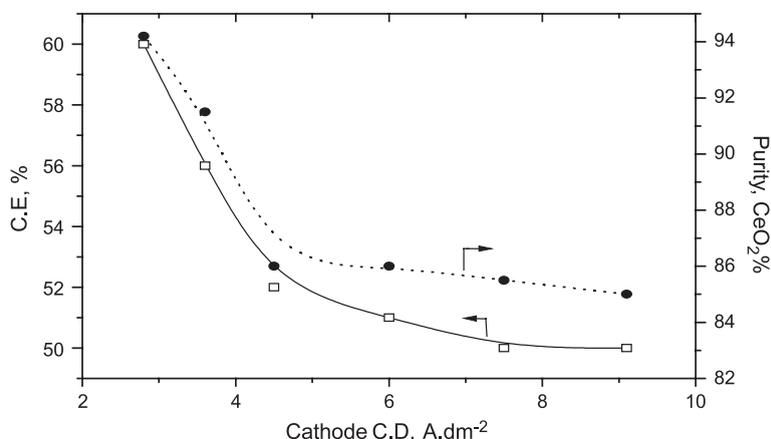
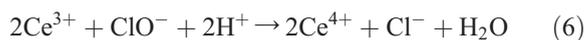


Fig. 4. Variation of current efficiency and purity of CeO₂ with cathode current density. Conditions: electrolyte concentration, 130 g/L; pH 6.5; temperature, 30 °C; anode current density, 500 A/m²; cathode rotation (peripheral velocity), 1.33 m/s.

The pH range between 6.5 and 6.8 is the most favourable range for the chemical reaction [reaction (5)] involving the hypochlorous acid and hypochlorite to produce chlorate provided the temperature is between 25 and 30 °C. The free hydroxide present at higher pH may lead to contamination with the Ce(OH)₃. These conditions indicate that the oxidation of cerium(III) to cerium (IV) by hypochlorite occurs due to the following reaction:



and the cerium (IV) is precipitated as Ce(OH)₄.

Chlorine evolution is a facile reaction, and an anode current density has only the effect of suppressing the competing oxygen evolution reaction during chloride electrolysis. The rate of evolution of oxygen is higher when the chloride concentration decreases below 1 M in the case of sodium chloride electrolysis. As the chloride concentration is much higher in the present instance, the anode current density used in all these experiments was 500 A/m².

The effect of cathode current density on the formation of ceric hydroxide is presented in Fig. 4. At higher cathode current densities, the concentration of hydroxide at the cathode surface layer increases,

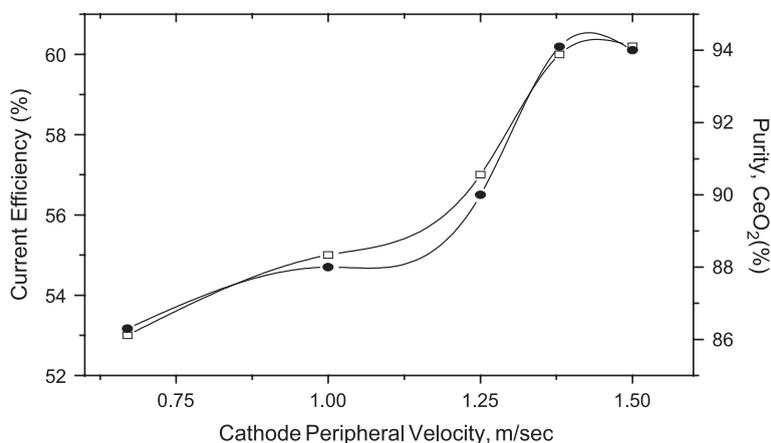


Fig. 5. Variation of current efficiency and purity of CeO₂ with cathode peripheral velocity. Conditions: electrolyte concentration, 130 g/L; pH 6.5; temperature, 30 °C; anode current density, 500 A/m²; cathode current density, 300 A/m².

and the cerium deposits as hydroxide on the cathode surface, decreasing the cathode efficiency and product purity. As was mentioned earlier (Vasudevan et al., 1992b), this also enhances the cell voltage and the electrolyte temperature. Both the purity and the efficiency are higher below 300 A/m^2 .

The deposition of the ceric hydroxide layer and its tendency to reduce to Ce(III) have been found to be minimized when a rotating cathode is employed. This is due to the distribution of the hydroxide formed at the cathode and decrease in the pH at the cathode surface. The precipitation pH of cerium is about 7.0–7.2 (Seaborg, 1994), therefore, the speed of cathode rotation has to be maintained in order to maintain the surface pH below 7.2. As seen in Fig. 5, while increasing the rotation speed, the efficiency is increased, but the purity levels off above 1.33 m/s. Similar observations were reported in the electrolytic preparation of alkaline earth metals (Vasudevan et al., 1992a,b).

4. Bench scale studies

The data obtained from the laboratory scale experiments were confirmed by scaling up the cell capacity to 15 A. A stainless steel tank [0.35 (L)×0.25 (b)×0.25 m (h)] was fitted with a PVC cover having suitable holes to introduce anode, cathode, thermometer and the electrolyte and acted as the cell. The anode was again a cylindrical titanium mesh [0.15 (dia)×0.25 m (h)] coated with noble metal oxides ($\text{RuO}_2/\text{TiO}_2/\text{SnO}_2$ based mixed oxides), while the cathode was a cylindrical stainless steel tube (SS304) [0.075 (dia)×0.38 m (h)] closed at the bottom and fitted to a rotating assembly (Vasudevan et al., 1992a). The cathode was positioned at the centre of the anode assembly at an interelectrode distance of 1 cm. Fig. 6 shows a sketch of the cell. Electrical connection to the cathode was given through mercury contained in a cup attached to the top end of the rotating shaft.

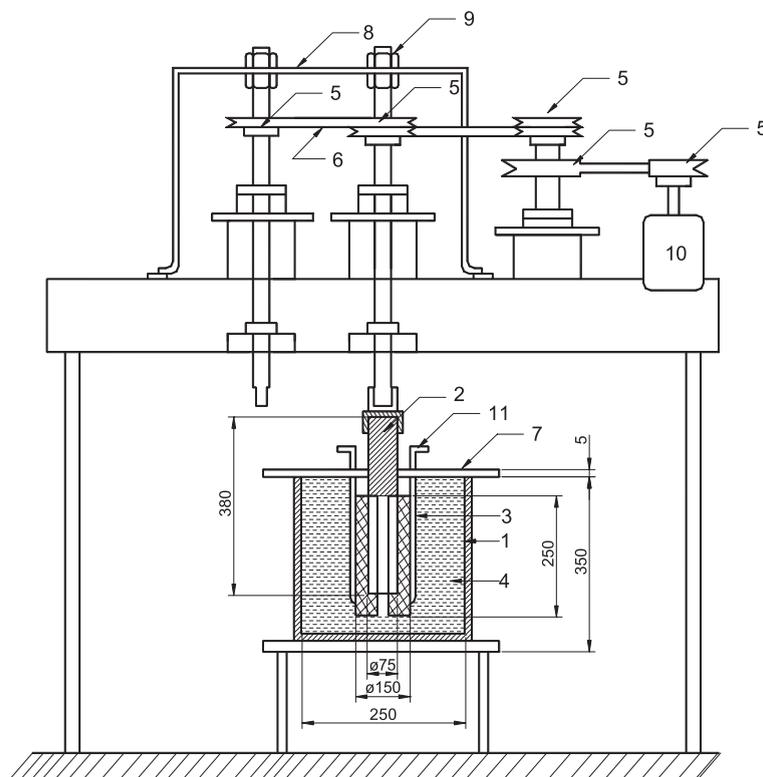


Fig. 6. A sketch of 15 A cell. (1) Stainless steel tank, (2) stainless steel cathode, (3) anode, (4) electrolyte, (5) pulleys, (6) V-belts, (7) PVC cover, (8) copper bus bar, (9) mercury cup, (10) 0.5-hp motor and (11) anode terminal.

Regulated DC was supplied from a rectifier (0–25 V, 100 A). The electrolysis was carried out under conditions optimized with the laboratory scale study. Each batch of electrolysis used 16 L of the mixed rare earth chloride solution, and the cell was operated at 15 A and ambient temperature. Each batch was operated continuously for over 90 h, and the average cell voltage ranged from 2.8 to 3.1 V. At the end of the electrolysis, the solid product obtained was centrifuged and washed free from chloride and dried at 110 °C. During three batches of electrolysis, the overall current efficiency and purity of the product were consistent at about 60% and >95%, respectively, with an energy consumption of 3.5 kWh/kg of CeO₂. The electrochemical process described herein is thus feasible.

5. Conclusions

The electrochemical separation of cerium from mixed rare earths was studied both in laboratory and bench scale cells. A rotating cathode is essential to avoid precipitation of the hydroxide on the cathode surface. Under appropriate conditions, it is possible to achieve current efficiencies as high as 60% at an energy consumption of about 3.5 kWh/kg of CeO₂. The purity of the product was >95%. By controlling the cathode rotation speed and surface pH below pH 7.2, the possibility of precipitating other metal ions like La, Nd, etc. is avoided. Better control of pH is likely to improve the CeO₂ purity, but for electronic grade product, further purification using solvent extraction is necessary.

Acknowledgement

The authors wish to express their sincere gratitude to Prof. A.K. Shukla, Director, Central Electrochemical Research Institute, Karaikudi-630 006, for his

permission to publish the paper. Thanks are also due to Sri. N.S. Narayanan, CGM, and Dr. V.R. Nayar, DGM, Indian Rare Earths Limited, Udyogamandal 683 501, for their enthusiastic encouragement, supply of raw material and also analytical support during the course of the study.

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