Third Arab Conference on the Peaceful Uses of Atomic Energy, Damascus 9 - 13 Dec. 1996 AAEA

Separation of Cerium (III) From Egyptian Monazite By Oxidation To Cerium (IV)

M.M. Ali(*), M.S.El-Alfy, M.A. Zayed**, K.A. Rabie,*
*N. El-Hazek and H.F. Aly**
Nuclear Materials Authority, Cairo, Egypt,
*Atomic Energy Authority, Cairo, Egypt,
**Cairo University, Faculty of Science, Cairo, Egypt.

خلاصة

يعتبر عنصر السيريوم من العناصر الإقتصادية الهامة التي لها تطبيقات عديدة وتمثل أكبر نسبة من العناصر الأرضية النادرة التي تستخدم في مجالات صناعية مختلفة. كذلك يعتبر عنصر السيريوم المكون الأساسي في عجينة الأرضيات النادرة الناتجة من الموناريت المصري حيث يمثل 45٪ منها وعليه فإن فصل هذا العنصر فصلاً كاملا من هذه العجينة له أهمية من النحية الإقتصادية علاوة على الناحية الفنية حيث يمكن بعد ذلك فصل العناصر الأرضي النادرة من بعضها البعض برطيق أكثر سهولة .

يقدم هذا البحث طريقة مطورة لفصل السيريوم كمياً من العناصر الأرضية النادرة الأخرى من عجينتها الناتجة من المونازيت المصري وذلك بواسطة أكسدة السيريوم في وسط يحتي على خليط من حمض الهيدروليك المخففين بواسطة بودرة التبييض البخارية. وقد تم دراسة وفحص العوامل المختلفة التي تؤثر على عملية أكسدة السيريوم لترسيبها كمياً وفصلها من لعناصر الأرضية الأخرى .

Abstract

The lanthanides hydrous oxides produced from the Egyptian Monazite contain about 45% cerium of the total lanthanides. The high concentration of Ce in this matrix complicates separation of different lanthanides from each other. In this paper a method was developed to separate cerium quantitatively from the lanthanide cake produced from Egyptian Monazite by precipitating tetravalent cerium from other trivalent lanthanides by oxidation of Ce (III) with bleaching powder from dilute solution of nitric - hydrochloric acids mixture. The different parameters affecting the separation were studied in details.

Introduction

Egyptian Monazite contains on the average 50% lanthanide oxides . In a pervious early work by Saleh [1] lanthanide oxides cake was successfully produced. This cake was found to contain around 45% cerium. Separation of trivalent lanthanides from such cake required quantitative removal of cerium. Conventional methods for separation of cerium from trivalent lanthanides are mainly based on precipitation of Ce (IV) from slightly acidic medium from the lanthanides solutions with suitable oxidising agent. Air oxidation with heating oxidised not more than 84% of cerium [2]. Peroxide oxidation was not effecient, less than 90%, with the hazardous of using peroxides [3].

Previous efforts to separate cerium from Egyptian Monazite succeeded only to remove not more that 80% of cerium [4,5].

Precipitation of tetravalent cerium from trivalent lanthanides solutions is based on the fact that the latter valency state resist hydrolysis than the tetravalent cerium ions [6,7]. Consequently, ceric salts are directly precipitated leaving trivalent lanthanides state in solution. Based on this concept, the present work was directed to investigate the oxidation of Ce (III) to Ce (IV) from nitric or hydrochloric acid medium and their admixture by commercial bleaching powder and find the most favorable conditions for Ce (IV) precipitation. Further, to apply this conditions on the lanthanide oxides cake of Egyptian monazite and develop a method for removal of Ce from this cake.

Experimental

The lanthanides cake was produced from Egyptian monazite according to the method developed by Saleh [1].

Commercial bleaching powder was used to oxidize Ce (III) to Ce (IV) in the matrix. The amount of active hypochlorite in bleaching powder was estimated in terms of active chlorine. This was carried out by titration with a standard sodium arsenite solution using starch and potassium iodide as indicator [8]. The amount of sodium arsenite consumed as related to the hypochlorite is given by the following equation:

$$Ca(OCl)Cl + Na_3AsO_3 = Na_3AsO_4 + CaCl_2$$

It is found that the bleaching powder used contains 37% ± 1 of available chlorine.

Oxidation processes:

With the objective of removing cerium as the major constituent in the lanthanides cake, the following conventional methods for oxidation of cerium to cerium (IV) were first carried out followed by bleaching powder method. In all cases, 5.0 g of the lanthanides cake (REO) was taken, unless other wise stated.

a- Mixed lanthanide hydroxides were dissolved in nitric acid and separation of heavy lanthanides from light lanthanides were carried out using 0.5 ml of H_2O_2 to reduce Ce (IV) to Ce (III) followed by addition of sodium sulfate [8]. A batch of light lanthanides sulfates was then precipitated with NaOH [9]. The precipitated light lanthanides were filtered off, washed thoroughly with water, dried and air oxidized in an oven at 125°C for 24 hours. This process separates only 82% of tetravalent cerium.

b- Two similar batches of mixed lanthanide hydroxides including Ce were air oxidized in oven at 140°C for 30 hours and at 180°C for 10 hours respectively. The first batch gives 72% and the second batch gives only 48 % of tetravalent cerium.

c - Oxidation of cerium by bleaching powder was investigated in details aiming at quantitative precipitation of Ce (IV) and solubilization of accompanied trivalent lanthanides in solution. 1.0 M nitric and hydrochloric acids solutions were used to dissolve trivalent lanthanides and keeping the less basic ceric hydroxides insoluble. In all cases, 5.0 g from the oxides cake was suspended in 250 ml of distilled water. Different amounts of 0.1 M HNO_3 and/or HCl were added at room temperature to the well stirred suspension of the oxides cake. After two hours stirring, the pH was determined and adjusted to 0.1-2.5 followed by heating for 10 minutes. Both the filtrate and precipitate were analyzed for cerium and trivalent lanthanides. Similar series of experiments were performed using different quantities of bleaching powder, and heating at different time intervals (10-60 min).

Analysis:

Cerium and different lanthanides were determined by different methods related to the matrix present. These methods are summarized as follows:

a- The determination of Ce oxidized in the dry cake was carried out by dissolving 0.2 g of the sample in 1:1 H_2SO_4 solution followed by boiling and filtration. The oxidized tetravalent Ce in the filrate was then determined by titration against standardized solution of ferrous ammonium sulfate using ferrion as indicator [10].

b- After leaching lanthanides hydrous oxides cake by (1.0M HCl, 1.0 M HNO_3 or 1:1 HCl-HNO_3 acid mixture), Ce was determined after adjusting the solution to 1.0 N H_2SO_4, addition of 0.5 mg $AgNO_3$ and 25 mg of potassium persulphate followed by boiling for 5 min., cooling and diluting to a known volume and finally measuring the absorbance at l = 320 nm, using double beam Perkin Elmer spectrophotometer.

c - The total lanthanides were determined using the arzenazo (III) method as previously reporte [11].

d- Determination of trace amounts of individual lanthanides including Ce was carried out by total reflection X-ray fluorescence spectrometry (TXRF). Reliable quantification was carried out using an internal Se standard. The TXRF is free from matrix effects and calibration is based on straight line where the slope and sensitivity solely dependent on the respective elements. This method is characterized by high sensitivity, low detection limits and multi-element determination [12].

Results and Discussion

As given in the experimental, use of H_2O_2 or air oxidation produced less than the 85% percent oxidation. This shows the unsuitability of these methods for quantitative removal of Ce from the lanthanide oxides cake of monazite.

Therefore, the different factors affecting oxidation and precipitation of cerium from trivalent lanthanide oxides mixture were investigated. This parameters includes the effect of the amount of bleaching powder, the hydrogen ion concentrations, the dissolving medium and temperature.

In Table (1) and figure (1), the dissolution of the dried hydrous oxides cake (5.0 g) in 1.0 M HNO3 and 1.0 M HCl was first performed in absence of bleaching powder. It is found that by decreasing the pH of both solution, thamount of dissolved lanthanides increases specially when the pH of the solution is less than 1.3. In addition, from the same acid medium the % RE_2O_3 dissolved is higher than that of cerium, a result which indicates that a certain amount of cerium in the lanthanide oxides cake is peresent with the tetravalent state of cerium. Further, dissolution of trivalent lanthanides and cerium is more in HNO_3 medium than in HCl medium.

The effect of addition of different amounts of bleaching powder on cerium oxidation and trivalent lanthanide oxides dissolution from nitric or hydrochloric acids media is investigated at various pH values (0.1-2.5). Figures [2,3] show the effect of the quantity added of bleaching powder on the percent cerium dissolution (dealing with cerium oxidation profile in terms of percent cerium dissolution) and trivalent lanthanides leaching from solutions of different pH values. From these figures, it is clear that the dissolved amount of lanthanides and cerium oxides decrease with increasing of bleaching powder up to 5.0 g per 5.0 g REO . This means that the percent cerium oxidized in both acid media increases with the increase of the quantity added of bleaching powder. Also, the amount of trivalent lanthanide oxides dissolved in nitric acid in the presence of bleaching powder is found to be higher than that dissolved in hydrochloric acid medium.

It is found also that the increase of heating interval plays a very important role in enhancing the percent cerium oxidation (lower dissolution values) and heating time of 30 min gives more better cerium oxidation results (less dissolution) than 10 and 20 minutes heating time under the same conditions. The changes in heating interval give no significance changes in the dissolution of trivalent lanthanide hydrous oxides. Cerium oxidation results, in terms of percent cerium dissolution at different pH values by addition of 5.0 g bleaching powder and at different heating intervals in nitric and hydrochloric acid solutions are represented in Figure (4).

Figures (2-4) show that the best oxidation results for cerium (less dissolution) using bleaching powder were obtained when using 5.0 g of bleaching powder with 5.0 g of the oxides cake. The most suitable working pH values are ranged from 1.3 to 1.5 and heating for 30 minutes in hydrochloric or nitric acid solutions.

When using HNO_3 : HCl (1:1) acid mixture for dissolution of trivalent lanthanides better results, with respect to cerium oxidation and trivalent oxides dissolution, are obtained than when using single acid solution, Table (2).

Table (1) : Solubility of 5.0g dried dydrous oxides in 1.0 M HNO_3 and HCl acid solutions (10 min. heating at 140°C after 2 hours stirring)

1.0 M HNO_3				1.0 M HCl			
pH before heating	pH after heating	percent of dissolved oxides to the total.		pH before heating	pH after heating	percent of dissolved oxides to the total.	
		Cerium	RE_2O_3			Cerium	RE_2O_3
2.5	4.5	21.9	57.5	2.5	4.7	18.1	45.5
2.0	4.4	28.1	58.8	2.0	4.7	19.8	46.4
1.5	4.2	31.8	59.6	1.5	4.6	24.4	47.0
1.3	4.2	36.4	62.2	1.3	4.5	26.2	49.2
1.0	4.0	48.3	72.3	1.0	4.2	31.4	60.2
0.8	4.0	54.2	74.1	0.8	4.1	32.9	67.6
0.5	3.7	67.7	84.9	0.5	3.8	47.3	73.3
0.1	2.9	75.3	93.8	0.1	2.8	59.3	86.7

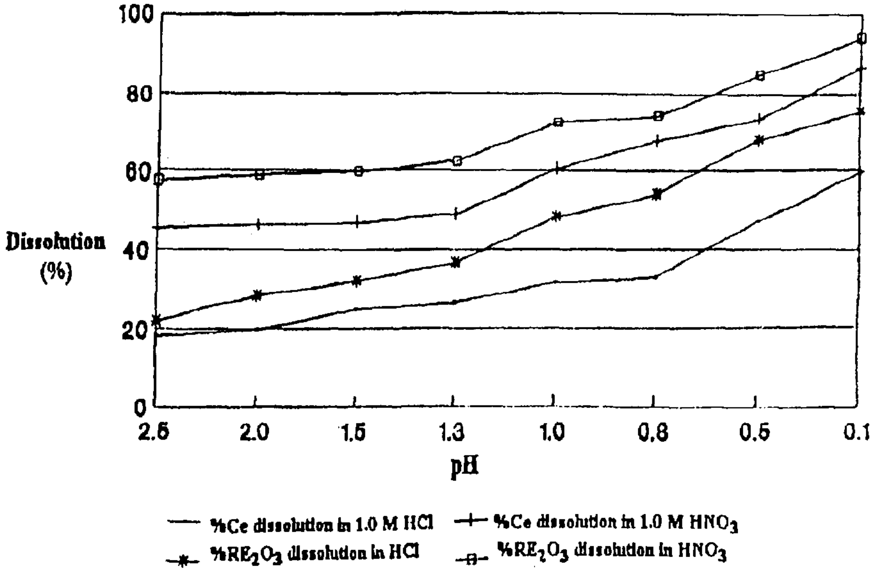

Figure (1) : Effect of pH on the percent dissolution of Ce and trivalent lanthanide oxides in 1.0 M HNO_3 and HCl acid solutions without bleacing powder

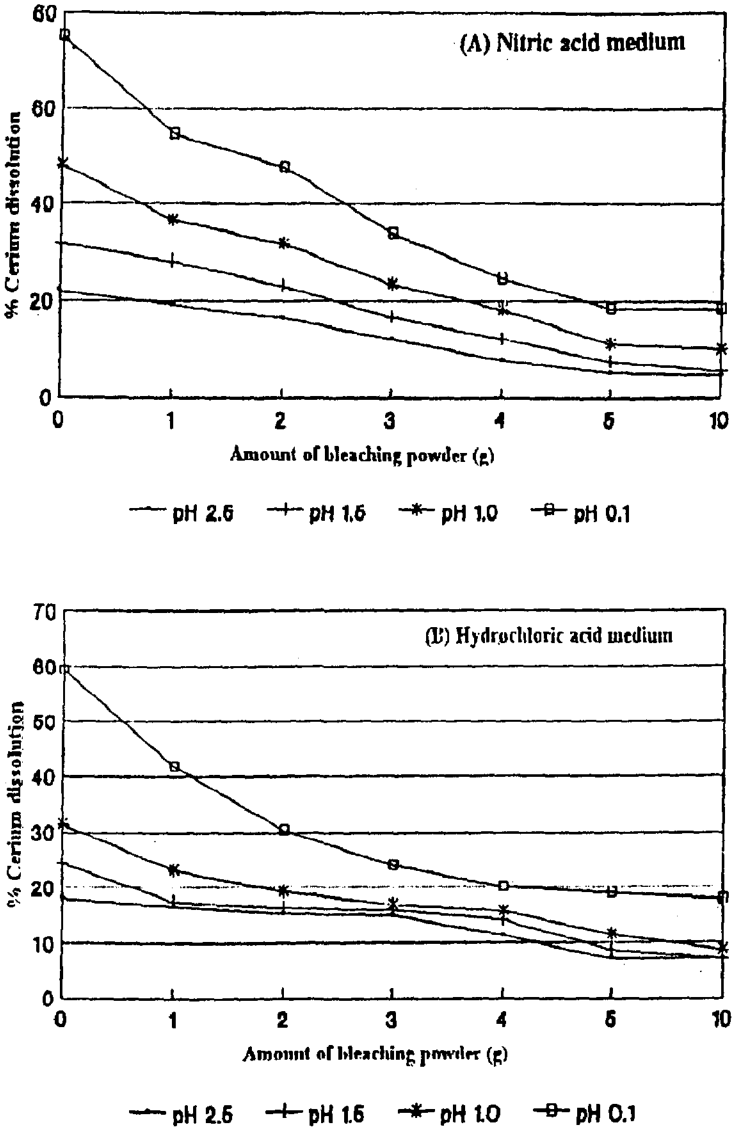

Figure (2) : Effect of bleacing powder on the percent Ce dissolution at different pH values after 2 hours stirring and 10 min. heating at 140°C in :
(A) 1.0 M HNO_3 and
(B) 1.0 M HCl acid solutions

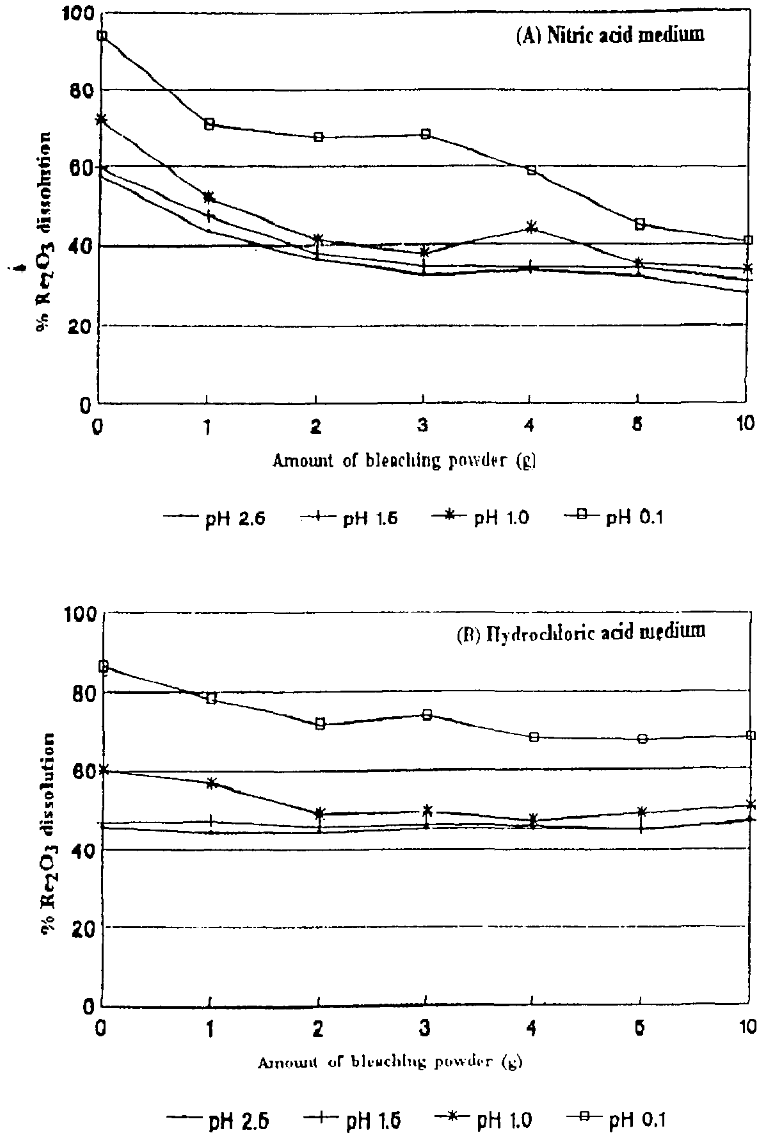

Figure (3) : Effect of bleacing powder on the percent trivalent lanthanide oxides dissolution at different pH values after 2 hours stirring and 10 min. heating at 140°C in :
(A) 1.0 M HNO_3 and
(B) 1.0 M HCl acid solutions

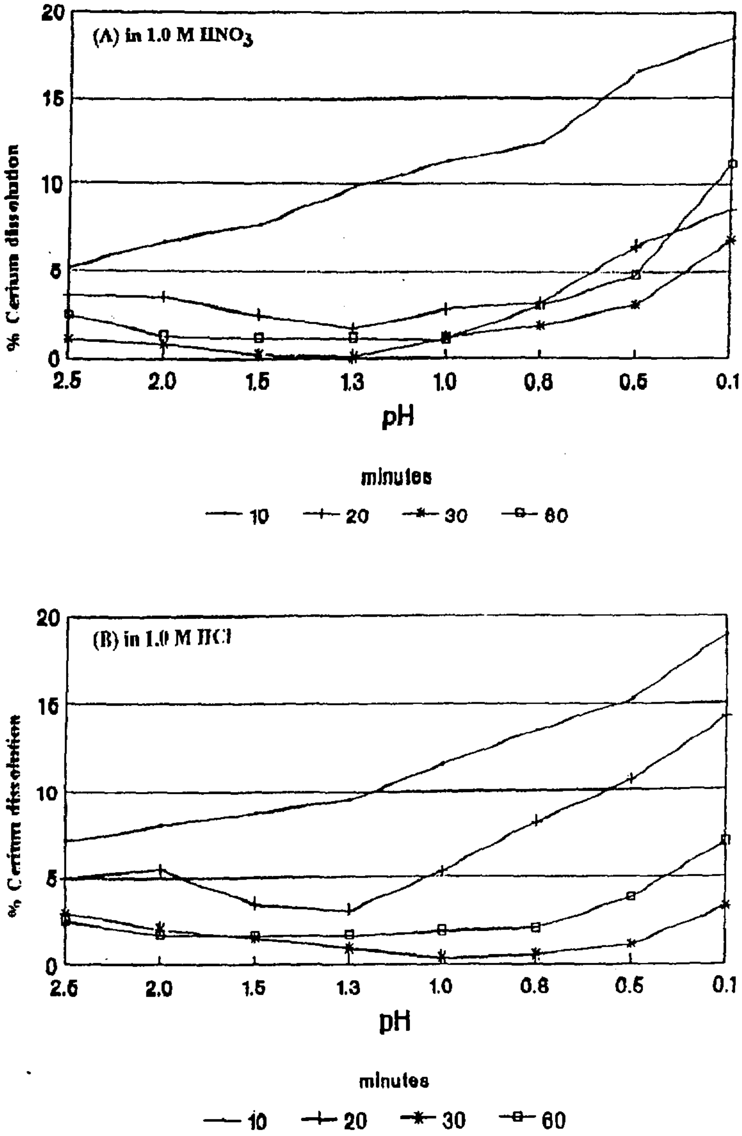

Figure (4) : Effect of heating interval on percent cerium dissolution at different pH values using 5 g hydrous oxides cake and 5 g bleacing powder after 2 hours stirring :
(A) 1.0 M HNO_3 medium
(B) 1.0 M HCl medium

To assess the quality of oxidation and separation process, selected experiments which give the best results, are repeated with subsequent complete analysis of the different elements in solution by TXRF. The different experiments and the results obtained are summarized in Table (2). From this table, it is clear that good precipitation of cerium (IV) is obtained when 5.0 g lanthanide oxides cake is leached with 1.0 M HCl solution at pH 1.5 in presence of 5.0 g bleaching powder with heating for 30 min at 120°C after 2hrs stirring (experiment 2). When nitric acid is used (experiment 4) instead of HCl, better precipitation of Ce (IV) is achieved. However, a few ppm of Ce are identified in solution. When equal volumes of 1.0 M HCl and HNO_3 acids are used as a mixture instead of HCl or HNO_3 alone for leaching the cake and under the same experimental conditions (experiment 5), Ce (IV) is completely precipitated and is absent in solution (filtrate). Experiments (1) and (3) of table (2) are carried out under the same experimental conditions of experiments (2) and (4) respectively but without addition of bleaching powder.

Table (3) summarizes the results obtained for treating 100 g sample of lanthanide oxides cake (upscaling) using the same experimental conditions of experiment (5). The analysis of the filtrate after Ce separation is given in column (1) of Table (3). It is clear from this table that no cerium is present in the filtrate i.e complete cerium removal under upscaling conditions is achieved with solubilization of most of the trivalent lanthanides other than cerium was obtained. The analytical composition of the precipitated cerium is given in

Table (2) : Total reflection X-ray fluorescence measurements. (all values are in ppm)

Element	Expt. 1	Expt. 2	Expt. 3	Expt. 4	Expt. 5
Se stand	1.000	1.000	1.000	1.000	1.000
Y	4.450	7.775	7.850	1.000	13.58
La	118.8	111.0	141.3	57.75	123.0
Ce	247.5	14.70	148.5	1.250	ND
Pr	14.70	14.57	19.67	6.050	18.15
Nd	59.00	68.75	86.50	19.70	96.25
Gd	27.50	4.000	5.35	0.625	5.750
Ti	ND	ND	ND	ND	ND
Dilution	1000	1000	1000	1000	1000

ND: Not detected.

column (2) of Table (3). Form this analysis, it is found that the main impurities precipitated with cerium concentrate are thorium and uranium together with small percent of other lanthanides. To separate U and Th impurities, the cerium cake is completely dissolved in concentrated hydrochloric acid and precipitated at pH 5.8, column (3) of Table (3) gives the analysis of the filtrate which indicates that cerium present in solution is completely free from Th and U. The cerium in such filtrate is precipitated at pH 8.3 and the filtrate is analyzed, column (4) of Table (3). From this analysis it is clear that cerium free from Th and U is quantitatively precipitated via its complete oxidation using bleaching powder as an oxidizing agent.

Table (3) : Total reflection X-ray fluorescence measurements (all values are in ppm)

Element	Expt. 1	Expt. 2	Expt. 3	Expt. 4
La	26.0	N.D	N.D	N.D
Ce	N.D	47.0	86.0	N.D
Pr	5.5	N.D	N.D	N.D
Nd	15.5	3.25	5.0	N.D
Sm	3.5	0.5	N.D	N.D
Eu	1.5	N.D	N.D	N.D
Gd	1.5	N.D	N.D	N.D
Y	2.0	0.5	2.0	N.D
Th	N.D	9.5	N.D	N.D
U	N.D	5.0	N.D	N.D
Dilution	**10000**	**10000**	**10000**	**10000**

N.D.: Not Detected.

Conclusions

In conclusion, cerium is quantitatively concentrated and separated from Egyptian monazite by leaching the monazite lanthanide oxides cake using 1.0 M acid solution of 1:1 HCl and HNO_3 in presence of bleaching powder after two hours stirring and 30 minutes heating around 120°C. Based on 5.0 g sample, the produced cerium concentrate contains 100% of the cerium beside 26% of the trivalent lanthanide's contents of the original lanthanide oxides cake. Upscaling the experiment with a starting material of 100 g sample of lanthanide oxides cake, a cerium cake is separated in a cerium concentrate containing 100% of the cerium with 4% of trivalent lanthanides other than cerium and contaminated with Th and U. Cerium concentrate free from Th and U is obtained after treatment of the cerium cake by complete acid dissolution and selective precipitation of Th and U at pH 5.8 then precipitation of cerium at pH 8.3.

References

[1] Saleh, A.F., UARAEE Int Report/3, Cairo, Egypt, (1966).

[2] Farag, A.K.A.K., Recovery of Thorium, UraniumCerium from Egyp Monazite

[3] Villani, F., ¢ Rare Earth Technology and Applications ¢. Academic Press, New York, USA, (1980).

[4] Gupta, C.K., and Krishnan, T.S., (eds.): ¢ RareEarths Applications and Technology ¢ Mater. Sci. Forum, 30, (1988).

[5] Bautista, R.G., and Wong, M.M., (eds.): ¢ Rare Earths ¢. Warrendale, PA, the Minerals, Metals and Materials Society, (1988).

[6] Busev, A.I., Tiptova, V.G., Ivanov, V.M., ¢ Analytical Chemmistry of Rare Elements ¢ , MirPublishers, Musco, (1981).

[7] Gupta, C.K., and Krishnamurthy, N., ¢ Extractive Metallurgy of Rare Earths ¢, Int. Materials Rev., Vol. 37 No. (5), Bhabha At. Research Centre, Bombay, India, 233 - 235, (1992).

[8] Mellor, J.W., ¢ AComprehensive Treatise Inorganic Chemistry ¢, Vol. II, Longmans Green and Co. Inc., London, (1960).

[9] Gschneider, K.A., Jr., and Ellis, T.W., ¢† Pure Rare Earth Metals for Today s and Tommorrow s Advanced Technologies ¢ ; Ames Lab., and the Dept. of Materials Science and Engineering, Twoa state University, Ames, Iowa, 50011 - 3020, USA, Edited by H.Y. Sohn, the Minerals, Metals and Materials Society, (1994).

[10] Bassett, J., Deany, R.C., Jeffery, G.H. Mendham,J., ¢ Vogel s Text Book of Quantitative Inorganic Anorganic Analysis ¢ , ELBS and Longman, London, (1984).

[11] Marczenko Spectrophotometric Determination of Elemments ¢ John Wiley and sons Inc., New York, (1986).

[12] Klockenkamper, R., and Alex Von Bohlen, J.Anal. Atomic Spectroscopy, Vol. 7, pp 237-279, (1992).