Russian Journal of Applied Chemistry, Vol. 75, No. 8, 2002, pp. 1357–1359. Translated from Zhurnal Prikladnoi Khimii, Vol. 75, No. 8, 2002, pp. 1384–1386.

BRIEF COMMUNICATIONS

On Production of Cerium Dioxide

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Received March 11, 2002

Abstract—The possibility of obtaining cerium dioxide by recovery of Ce(IV) phosphate from acid nitrate solutions with subsequent conversion of Ce(IV) phosphate to Ce(III) oxalate was studied.

Cerium is the most widespread and demanded representative of rare-earth elements (REE). Its content in most of the concentrates being refined exceeds 50 wt %. As a rule, Ce(III) is isolated from an REE mixture through its oxidation to Ce(IV) and subsequent separation by extraction or precipitation with account of differences in the pH of precipitation of mixture components [1, 2].

It is impossible to completely separate cerium(IV) from other REEs by precipitation techniques owing to the close pH values of their precipitation and the considerable adsorptivity of the resulting precipitates. Purer cerium compounds can be obtained by precipitation of Ce(IV) phosphate, which is precipitated at higher acidity than triply charged REEs. Processes of this kind have been proposed for recovery of cerium from monazite [3] and a phosphate concentrate from apatite [4]. A drawback of the phosphate procedure is the complexity of phosphorus(V) removal.

A procedure for processing REE phosphates, based on their conversion to oxalates, has been proposed earlier [5, 6]. Its applicability to the production of cerium dioxide was assessed in the present study.

EXPERIMENTAL

Cerium was oxidized in an acid nitrate medium on a platinum anode. A solution prepared from loparite was used for oxidation. It contained 300 g l^{-1} of Ln_2O_3 and 164 g l^{-1} of Ce_2O_3. After the oxidation the solution contained Ce(IV) in the form of CeO_2 (42 g l^{-1}). The cerium(IV) content in solutions was determined by titration with Mohr's salt $(NH_4)_2Fe(SO_4)_2$. Cerium(IV) phosphate was precipitated from 2–3 N HNO_3 solution by addition of ammonium hydrophosphate $(NH_4)_2HPO_4$. Almost complete precipitation was attained by addition of one mole of PO_4^{3-} per one mole of CeO_2, which corresponds to precipitation of basic phosphate $CeOHPO_4$. This precipitate was filtered off, washed by repulping in 1 N HNO_3 at a solid-to-liquid phase ratio (s : l) of 1 : 3 and treated with oxalic acid in 1.5 N HNO_3 at 80°C for 1 h (s : l = 1 : 3). The conversion to the oxalate occurs by the following reaction:

$$2Ce(OH)PO_4 \cdot nH_2O(s) + 4H_2C_2O_4(l)$$
$$\rightarrow Ce_2(C_2O_4)_3 \cdot 10H_2O(s) + 2H_3PO_4 + 2H_2O + 2CO_2.$$

Precipitated oxalates were isolated, washed with 1 N HNO_3, and calcined at 900°C. The impurities in cerium dioxide were determined by X-ray fluorescent analysis. The results of the experiments are presented in the table.

As a rule, 75–90% concentrates are produced by single-stage precipitation of Ce(IV) hydroxide, carbonate, or basic nitrate [3]. Cerium samples obtained by precipitation of Ce(IV) phosphate are significantly

Composition of cerium dioxide obtained by recovery of $CeOHPO_4$

Recovery conditions		Impurity content, wt %				
HNO_3, M	Repulping	La_2O_3	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	P_2O_5
2	1	2.2	0.6	1.2	0.12	0.1
2	2	0.78	0.34	0.58	nd*	0.11
3	1	1.86	0.52	1.12	″	nd*
3	2	0.66	0.26	0.58	″	″

* Not determined.

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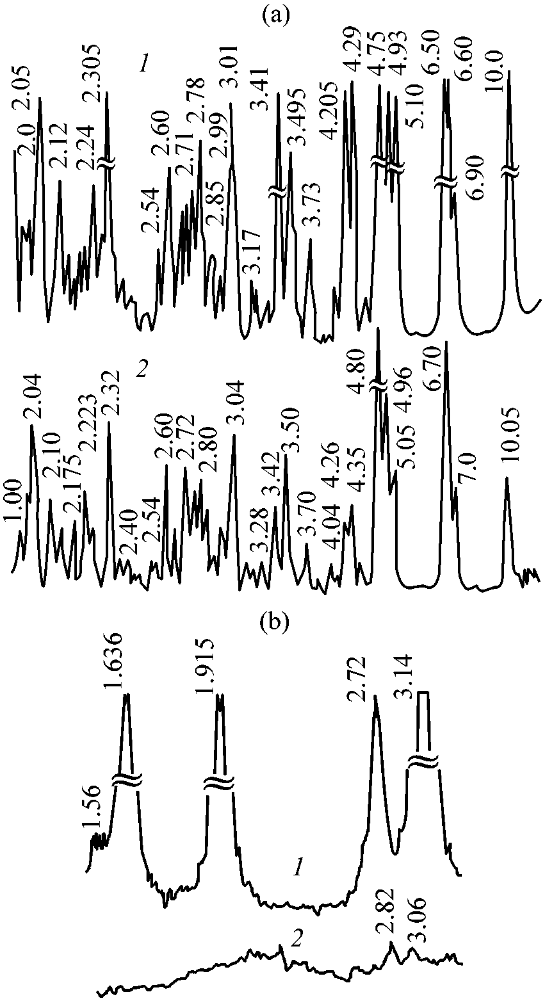

Fig. 1. X-ray diffraction patterns of oxalate samples obtained by conversion of (*1*) Ce(IV) and (*2*) Ce(III) phosphates. Sample: (a) initial and (b) after heat treatment at 250°C for 3 h.

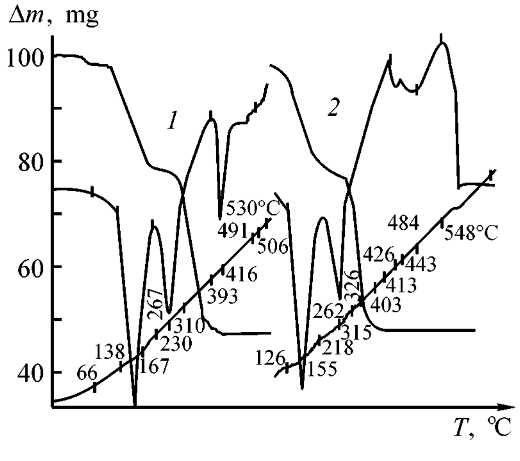

Fig. 2. DTA and weight-loss (Δm) curves for oxalates samples obtained by conversion of (*1*) Ce(IV) and (*2*) Ce(III) phosphates. (*T*) Temperature.

purer and can be used in various fields of technology. A required purity of cerium phosphate can be achieved by its reprecipitation, which can be used for recovery of cerium(IV) from acid solutions after its electrolytic oxidation, since the precipitation procedures involve solution neutralization. At the same time, the extraction recovery entails a considerable loss of the extractant because of its decomposition by Ce(IV), which is a strong oxidizing agent, and by hydrogen peroxide used for the reextraction.

It was found that oxalates obtained from Ce(IV) phosphate differ from those prepared by conversion of Ce(III) orthophosphate in their thermal behavior. Samples of Ce(III) oxalates were synthesized under similar conditions. The content of P_2O_5 in the samples under study was not greater than 0.1%. Although both kinds of oxalate samples have identical X-ray diffraction patterns (Fig. 1a) and thermogravimetric characteristics (Fig. 2), the oxalate obtained from Ce(IV) phosphate is converted to bright yellow cerium dioxide under heating at 250°C for 3 h, whereas the oxalate obtained from Ce(III) phosphate only loses water and becomes X-ray-amorphous (Fig. 1b) under the same conditions. It is converted to dioxide only at 410°C [7], and cerium(III) oxide is shown to form at 370°C [8].

Low-temperature forms of cerium dioxide are likely to be of practical importance, e.g., in catalysis [9, 10]. On the whole, the technology of cerium dioxide production with preliminary recovery of Ce(IV) phosphate is well applicable, because phosphate ions and most of oxalic acid can be recycled. Naturally, treatment of bulk precipitates of Ce(IV) phosphate presents difficulty, but advantages of the method are also obvious.

CONCLUSION

It was shown that cerium dioxide can be produced through preliminary recovery of Ce(IV) phosphate from acid nitrate solutions and its subsequent conversion to Ce(III) oxalate.

Differences in thermal behavior between cerium oxalates obtained by conversion of Ce(IV) and Ce(III) phosphates were found. In the first case, the product decomposes at low temperature (250°C) to form CeO_2.

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